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Laboratory Protocol for
Determining Fate of Waste
Disposed in Deep Wells

National Inst. for Petroleum and Energy Research
Bartlesville, OK

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

Feb 88

U.S. Department of Commerce
National Technical Information Service

NTIS

LABORATORY PROTOCOL FOR DETERMINING FATE
OF WASTE DISPOSED IN DEEP WELLS

by

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Prepared For
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The objective of the research was to develop a protocol to evaluate organic hazardous waste for mobility, adsorption, and degradation potential under simulated subsurface geologic reservoir temperatures and pressures. To achieve the objective three areas of work were addressed. The first area was an assessment of prior research conducted on deep-well organic waste disposal and areas where additional information on degradation, mobility, and ultimate fate is needed. The second area addressed the experimental conditions which are necessary to develop a laboratory protocol to determine the fate of deep-well disposed organic wastes. The third area was the development of the protocol itself. The laboratory protocol described in the report provides data needed to predict the fate of deep-well injected wastes. The knowledge is necessary to ensure that deep-well injected wastes do not contaminate ground waters.

KEYWORDS: *Hazardous materials, *Injection wells.

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DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Interagency Agreement Number DW89931947 to the National Institute for Petroleum and Energy Research, Bartlesville, Oklahoma. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document.

FOREWORD

The U.S. Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

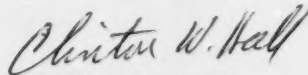
An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of the facilities, the Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rate of pollutants in the soil, the unsaturated zone and the saturated zones of the subsurface environment, including zones for deep-well injection of hazardous wastes; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, deep-well injection zones and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

Provisions of the Resource Conservation and Recovery Act (RCRA) require that by 1988 the Environmental Protection Agency (EPA) show that the disposal of specific wastes is safe to human health and the environment, or the practice of deep-well injection of hazardous wastes must be discontinued.

This report provides a protocol for evaluation of the degradation, interaction and fate of hazardous wastes injected into geologic reservoirs by deep wells, thus contributing to that knowledge which is essential in order for EPA to establish and enforce pollution control standards which are reasonable, cost effective and provide adequate environmental protection for the American public.



Clinton W. Hall
Director
Robert S. Kerr Environmental
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ABSTRACT

The objective of this research investigation was to develop a laboratory protocol for use in determining degradation, interaction, and fate of organic wastes disposed in deep subsurface reservoirs via disposal wells. Knowledge of the ultimate fate of deep-well disposed wastes is important because provisions of the Resource Conservation and Recovery Act (RCRA) require that by August 1988, the Environmental Protection Agency (EPA) must show that the disposal of specified wastes by deep-well injection is safe to human health and the environment, or the practice must be stopped. The National Institute for Petroleum and Energy Research (NIPER) developed this protocol primarily by transferring some of its expertise and knowledge of laboratory protocol relevant to improved recovery of petroleum; for example, (1) core analysis, (2) brine analysis, (3) oil analysis, (4) dynamic fluid flow systems, which simulate subsurface reservoir conditions, and (5) appropriately trained personnel.

This study was designed to investigate the adsorption properties of a specific reservoir rock which is representative of porous sedimentary geologic formations used as repositories for hazardous organic wastes. Phenol is the principal hazardous waste product that has been injected into the Frio formation; therefore, a decision was made to use phenol and sedimentary rock from the Frio formation; for a series of laboratory experiments to demonstrate the protocol. The developed protocol can be used to evaluate mobility, adsorption, and degradation of an organic hazardous waste under simulated subsurface reservoir conditions.

This report is submitted in partial fulfillment of Contract Number DW89931947 under the sponsorship of the U.S. Environmental Protection Agency through an interagency agreement between the U.S. Department of Energy and the U.S. Environmental Protection Agency. The report covers the contract period from December 16, 1986 to September 30, 1987, and the work was completed as of September 30, 1987.

TABLE OF CONTENTS

	Page
Disclaimer.....	ii
Foreword.....	iii
Abstract.....	iv
Tables.....	vii
Illustrations.....	viii
Nomenclature.....	ix
Acknowledgments.....	x
Introduction.....	1
Experimental Considerations.....	3
Development and Demonstration of Protocol.....	4
Dynamic Fluid Flow System.....	4
Core Samples.....	6
Core Preparation.....	9
Hazardous Wastes.....	9
Frio Brine System.....	10
Experimental Brine and Waste System.....	10
Fluid Flow System Operation.....	10
Static System.....	11
Fluids Tested.....	11
Results and Discussion.....	12
Desorption and Degradation Experiments.....	22
Observations.....	22
Recommendations for Future Use of Protocol.....	23
Core Analysis.....	23
Organic Hazardous Waste and Brine Analysis.....	23
Determination of Adsorption-Fluid Flow Method.....	23
Determination of Adsorption-Static Method.....	24
Conclusions.....	24
References.....	25
Appendix A. - Classification of Injection Wells.....	27
Appendix B. - Experimental Procedures.....	28
I. Core Preparation.....	28
Determine Brine Porosity of a Consolidated Core.....	28
1. Core Dimensions.....	28
2. Mount Core in Rubber Sleeve.....	28
3. Determine Dry Core Weight.....	28
4. Determine Saturated Core Weight.....	30
5. Determine Weight/Volume of Brine Reservoir.....	30
6. Calculate Porosity and Pore Volume.....	30
Calculations.....	32
7. Dispersion Experiments.....	32
Calculations.....	33
Terms Used.....	37
II. Core and Brine Evaluations.....	37
Inductively Coupled Plasma Analytic Methods.....	37
Summary of Method.....	37
Reagents and Standards.....	37
Sample Handling and Preservation.....	38

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Sample Preparation	38
Procedure	38
Calculation	39
Quality Control	40
Scanning Electron Microscopy (SEM)	40
X-ray Diffraction Analysis (XRD)	41
Sample Preparation	41
Semiquantitative Interpretation of Mineral Abundance	42
Calculations	43
Peak Identifications	43
III. Analysis Phenols and Phenol Degradation By-Products	45
Appendix C - Precision and Bias Statements for the Various Analytic Techniques	47
Appendix D - Quality assurance procedures for the experimental portion	50
Introduction	50
Project Discription	50
Project Organization and Responsibilities	50
Organization	50
Key Staff	52
Coordination with EPA	52
Quality Assurance Objectives	52
Analytical and Experimental QA Procedures	53
Core Sample Use/Preparation	53
Organic Contaminant Selection/Preparation	53
Analytic Procedures	53
Sample Handling	54
Instrument Maintenance	54
Inductively Coupled Plasma Spectrometer	54
Gas Chromatograph	55
Corrective Action	55
Appendix E. - Policy Statement for the National Institute for Petroleum and Energy Research	56
Quality Assurance Management	58
Responsibilities and Authority of Quality Assurance Office (DQAO)	58
Project Audits	58
Document Control	59
Quality Assurance Unit Control (Audit) Sample(s) Report.....	60
Quality Assurance Unit Inspection Report	61

TABLES

	<u>Page</u>
1. X-ray diffraction analysis of the Frio rock.....	9
2. X-ray diffraction analysis of the Cottage Grove rock.....	9
3. Organic compounds used in the equilibrium adsorption experiments and the concentration range used for each compound.....	10
4. Atomic absorption analysis of an input phenol solution and an effluent phenol solution.....	12
5. Analytic results for flow-through method using phenol.....	14
6. Rate constants for each compound tested at specific initial concentrations and temperatures.....	19
7. Calculated values of the coefficients of molecular diffusion for each compound in water at the temperature of interest.....	20
8. Constants F and n for the Freundlich isotherms shown in figures 6, 8, 9 and 10.....	21
9. Isothermic heats of adsorption calculated for each concentration of the compounds that were tested.....	22
B-1. Computer program for dispersion	36
B-2. Spacings for mineral identification	44
B-3. Typical operating conditions for chromatographic conditions	46
C-1. Atomic absorption precision and bias statements.....	47
C-2. ICP precision and accuracy data.....	48
C-3. GC accuracy and bias in reagent water.....	49
C-4. GC accuracy and bias in matrix water.....	49

ILLUSTRATIONS

	<u>Page</u>
1. Schematic of fluid flow apparatus.....	5
2. Detail of core mounting assembly.....	7
3. Stainless steel test cell.....	8
4. Freundlich isotherm for phenol using Frio core.....	13
5. Rates of adsorption of 1,2-dichloroethane and phenol.....	15
6. Freundlich isotherms of 1,2-dichloroethane on Cottage Grove.....	16
7. Freundlich isotherms of phenol on Cottage Grove.....	16
8. Rates of adsorption of phenol using Frio core.....	17
9. Rates of adsorption of 1,2-dichloroethane using a Frio core.....	18
B-1. Schematic diagram of core setup.....	29
B-2. Schematic diagram of brine reservoir.....	31
B-3. Computed curves for constant concentration injection and slug injection.....	35
D-1. Project organization and management.....	51

NOMENCLATURE

A	= Cross sectional area of core, cm^2
A_1	= Amount of solute adsorbed by the rock, mg/kg of rock
C	= Dimensionless concentration
C_1	= Solution concentration at any time, mg/liter
C^1	= Initial concentration, mg/liter
C^0	= Concentration of solute adsorbed on the surface, mg/liter
C^S_∞	= Final solution concentration in equilibrium with the solid, mg/liter
D	= Coefficient of molecular diffusion, cm^2/hr
F	= Constant of the Freundlich isotherm, from the intercept with the vertical axis
ΔG	= Gibbs free energy
H^0	= Partial molal enthalpy of the adsorbent in the liquid state
H^0_S	= Partial molal enthalpy of the adsorbate
ΔH_{iso}	= Isosteric heat of adsorption
K	= Adsorption rate constant, 1/hr
K_e	= Overall equilibrium rate constant
L^e	= Total length of core, cm
n	= Constant of the Freundlich isotherm, from the slope of the line
Q	= Influent flow rate of fluid, ml/hr
R	= Gas law constant, 1.987 cal/g-mole
t	= Time, hours
T	= Temperature, $^\circ\text{K}$, except where specified otherwise
$\emptyset$	= Porosity, fraction of total

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INTRODUCTION

The objective of this research was to develop a protocol to evaluate organic hazardous waste for mobility, adsorption, and degradation potential under simulated subsurface geologic reservoir temperatures and pressures. To achieve this objective three areas of work were addressed. The first area was an assessment of prior research conducted on deep-well organic waste disposal and areas where additional information on degradation, mobility, and ultimate fate is needed. Very little laboratory research relevant to the fate of deep-well disposed inorganic waste has been conducted.

The second area addressed the experimental conditions which are necessary to develop a laboratory protocol to determine the fate of deep-well disposed organic wastes. The work was performed in stages with refinements and evaluations made after each stage. Items considered included:

1. selection of the appropriate laboratory system;
2. selection of appropriate core samples, and core analysis methods;
3. selection of an appropriate brine system, and brine analysis methods; and
4. selection of the hazardous organic waste materials, and waste analysis methods.

The third area was the development of the protocol itself. The laboratory protocol described in this report provides data needed to predict the fate of deep-well injected wastes. This knowledge is necessary to ensure that deep-well injected wastes do not contaminate ground waters. It is imperative that every possible precaution be taken to ensure that deep-well injected wastes do not contaminate ground water, because it is estimated that 50 percent of the Nation's drinking water comes from ground water, that 75 percent of our cities obtain all or part of their water supplies from ground water, and that rural areas are 95 percent dependent on ground water as a source of water.

Appendix A describes the classification of the five types of injection wells. Results generated by this protocol should be useful in proving the fate of wastes injected into Class 1 wells. About 11 percent of all hazardous wastes are injected into deep subsurface geologic rock formations for disposal. The wells used for these injections in the United States are classified as Class 1, and their record of performance is good.

Possible mechanisms whereby injection of hazardous wastes might contaminate ground water aquifers include: (1) a surface spill followed by migration of the waste into ground water; (2) unplugged or incompetently plugged wells that penetrate the geologic zone into which the waste is injected providing an escape route whereby the waste can enter an overlying potable ground-water aquifer; (3) vertical fracturing of the injection and confining strata caused by excessive injection pressures whereby a communication channel allows the injected wastes to migrate to a fresh water aquifer; and (4) mechanical failure of the injection system such as

corrosion of surface pumps or pipes or subsurface tubing or casing which allows the waste to escape and migrate to a ground water aquifer.²

EPA, in their 1985 report to congress on hazardous wastes,³ described four major ways in which subsurface injection practices can cause fluids to migrate into underground sources of drinking water (USDWs). They are: (1) faulty well construction; (2) improperly plugged or completed wells in the zone of endangering influence; (3) faulty or fractured confining strata; and (4) lateral displacement.

Provisions of the Resource Conservation Recovery Act (RCRA) require that by August 8, 1988, the Environmental Protection Agency (EPA) must show that the disposal of specified wastes by deep-well injection is safe to human health and the environment, or the practice must be stopped. Knowledge of the long-term fate of these wastes in the injection zones is necessary to address the provisions.

Demonstration of the fate of wastes injected into subsurface rock formations requires knowledge of the behavior of the waste after injection. The interaction of the waste with other reservoir fluids and reservoir rock constituents such as silicates, carbonates, sulfates and clays must be known. Hazardous wastes often are complex mixtures, and when combined with other complex mixtures the interactions can increase factorially.

Development of appropriate methodology to determine the fate of hazardous organic wastes injected into deep-wells for disposal in subsurface geologic reservoirs represents formidable challenges to the scientist. Current knowledge of deep subsurface geologic reservoirs was established primarily by petroleum related sciences of geology, engineering, chemistry, physics, hydrology, etc. Subsurface reservoirs into which hazardous wastes are injected consist of sedimentary deposits, which are the same types of sediments from which petroleum is generated and produced.

The present study focused on relevant technology whereby the fate of hazardous organic wastes could be studied in the laboratory. It was determined that both a static system and a dynamic fluid flow-through core system should be used. The static system should be useful to establish longer term degradation information, and the dynamic system should provide knowledge pertinent to migration of the waste in the reservoir rocks. A state-of-the-art report¹ indicated that very little laboratory research has been performed concerning the fate of hazardous organic wastes in deep subsurface reservoirs.

Most deep geologic formations used for disposal of hazardous wastes consist of unconsolidated sands and sandstones, as exemplified by the Frio Formation. The minerals in these rock formations serve as sites for the adsorption of numerous organic compounds and thus retard or attenuate the migration of the hazardous organic waste from the injection zone. Shale and/or clay or silt dominant formations, which overlie many formations such as the Frio, serve as hydrocarbon traps and also should

serve to retard the vertical migration of injected hazardous wastes out of the injection zone. Because adsorption is significant in estimating the migration of injected waste constituents, methodology was developed to determine the equilibrium adsorption properties of organic compounds on formation rocks such as the Frio Formation at simulated subsurface conditions of 3,000 psi (20.7 MPa) and temperatures up to 140° F (60° C).

A large volume of laboratory results has been compiled on the adsorption of organic compounds onto numerous materials;¹ however, very few results are reported on the equilibrium adsorption properties of subsurface formation rocks. This work was designed to investigate the adsorption properties of a specific subsurface sedimentary formation rock because it is specific subsurface geologic formations into which hazardous wastes are injected for disposal. The dynamic fluid flow-through porous media equipment developed for this work should be applicable to many studies relevant to the flow and transport of injected wastes.

Many organic constituents are hydrophobic (water-disliking), and their movement in ground water systems is affected by sorption phenomena, where the solute (organic constituent) is transferred from the liquid or solvent phase (ground water) to the solid phase (rock or soil particles). This is a phase partitioning process called adsorption, and it may be fully or partially reversible (desorption). Many chemical and physical properties of both the solute and solid phases impact adsorption/desorption, and the physical chemistry of the phenomenon is complex.

Adsorption of a liquid hazardous waste, such as phenol, onto the minerals in a subsurface formation rock could cause the adsorbed waste constituent to be attenuated or retarded and not migrate in hazardous concentrations from the injection zone of a subsurface disposal well. Because adsorption is significant in estimating the migration characteristics of injected waste constituents, this study was designed to investigate quantitatively the equilibrium adsorption properties of specific organic hazardous wastes.

Adsorption can be categorized into three classes: exchange, physical, and chemical. Exchange occurs from the electrostatic attraction of ions or charged functional groups from the solute phase to the solid phase which possesses charged locations. Physical adsorption occurring between the phases is motivated by Van der Waals forces or electrostatic interaction between atoms and molecules.⁴ Chemical adsorption (chemisorption) is caused by a chemical reaction between the solute phase and the solid phase. Discrete occurrences of these classes are not common, and phase partitioning of a solute-solvent-solid system probably occurs where two or all three of the adsorption classes operate.

EXPERIMENTAL CONSIDERATIONS

After detailed consideration of various laboratory systems, it was decided to use both a dynamic flow and a static system. The dynamic flow system provides optimum information relevant to interactions between reservoir rock and selected organic hazardous wastes, whereas the static system provides necessary back-up information. The Frio Formation is the dominant geologic repository used for hazardous wastes disposal in the Gulf Coast area due to its lithologic characteristics. Since hazardous

organic wastes are injected into the Frio formation, it was decided that rock from a well drilled in this formation should be used. A dilute sodium chloride solution was used as the diluent in the initial demonstration and verification experiments.

Because phenol is the predominant organic hazardous waste injected into the Frio formation, it was selected as the compound to study in the first demonstration and verification experiments. The next compound selected was 1,2-dichloroethane. They are listed in Appendix VIII-Hazardous Constituents, Section 3001, RCRA, Federal Register, vol. 45 No. 98, May 19, 1980, page 33126. Their hazardous waste numbers are U188 and U077.

DEVELOPMENT AND DEMONSTRATION OF PROTOCOL

This experimental section consists of design details and operational methods for a dynamic fluid flow-through core system and a static system. Instrumentation and methods used for the identification of organic waste compounds and their degradation products also are described. Essential basic core evaluation techniques for an experiment of this type are described in appendix B and include: (1) basic core analysis, (2) scanning electron microscopy, and (3) x-ray diffraction. Evaluation of the amounts and types of organic materials and clays present in the core samples is needed to determine their effect upon adsorption, degradation, and transport of hazardous waste constituents. The dynamic flow-through system is capable of simulating a waste-disposal reservoir at various temperatures and pressure. A pressure of 3,000 psi (20.7 MPa) should affect the degree of permeability of the core sample tested, but should have no effect on adsorption or degradation. The dynamic flow-through units were designed, fabricated, and used at NTPER. Procedures for (1) core preparation, (2) core evaluation and brine evaluation, and (3) analysis of hazardous waste and hazardous waste degradation by-products are described in appendix B.

Dynamic Fluid Flow System

A diagram of the fluid-flow apparatus is shown in figure 1. The system resembles a high-pressure liquid chromatograph except that the chromatographic column is replaced by a core sample taken from a subsurface formation.⁵

To simulate reservoir pressure conditions, the core sample is encased in a high-pressure stainless steel cell. The cell is filled with fluid (usually water), which provides the means of simulating an overburden pressure on the core with the hydraulic pump. The core is physically separated from the overburden fluid by a rubber Hassler sleeve. A heating mantle around the cell provides simulated reservoir temperatures. Fluids used in the experiment are pumped through the core by a high-pressure, constant-rate pump, and the internal pressure of the system is adjustable using a pressure-control valve.

Figure 1 shows that samples eluting from the core may be collected via an automatic fraction collector, or may be diverted to an ultraviolet (UV)

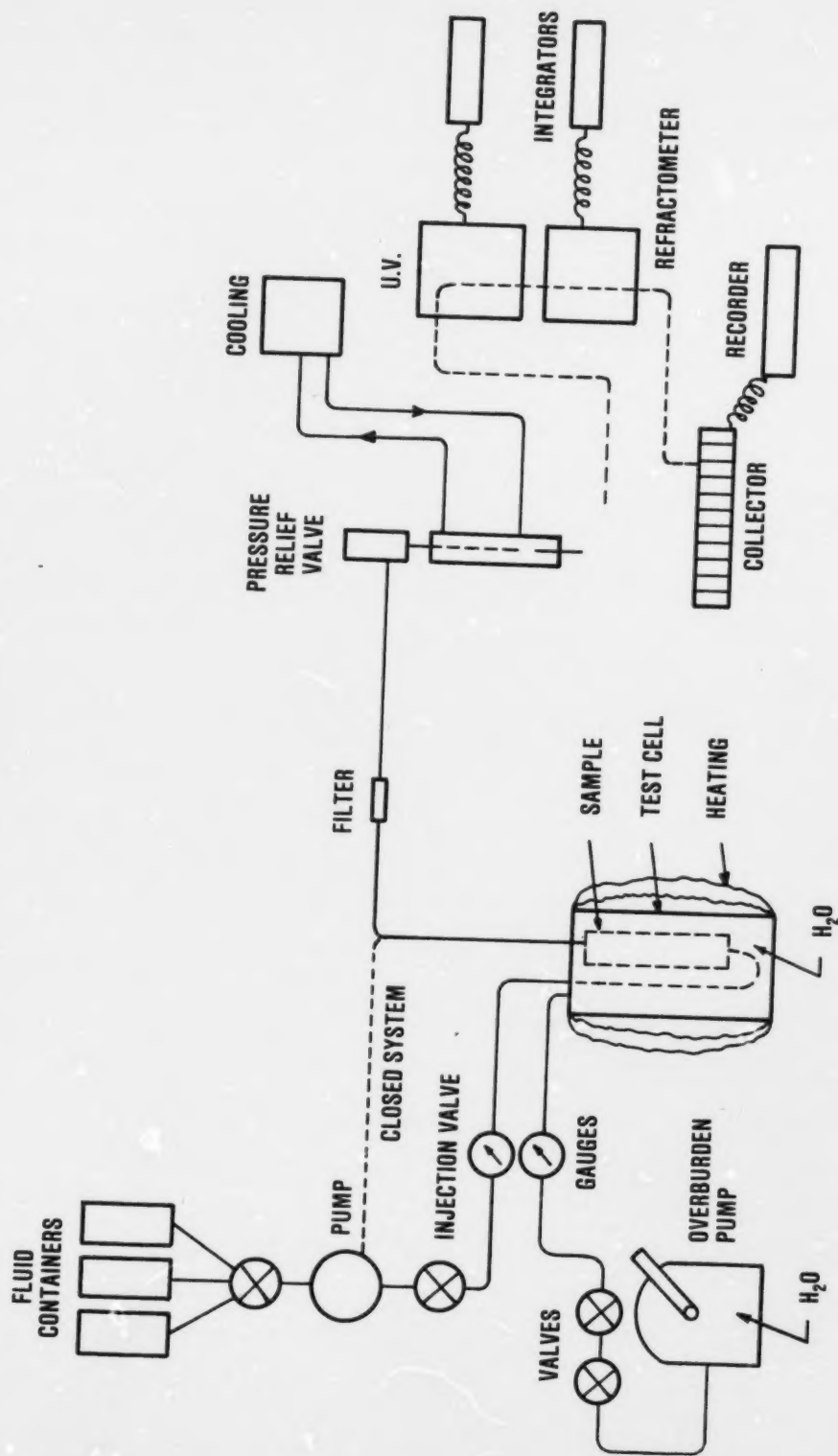


FIGURE 1. - Schematic of fluid flow apparatus.

spectrophotometer and/or refractometer for on-stream analysis. This arrangement permits the analysis of different simulated core floods, with the method of detection dependent upon the particular type of chemical being analyzed. Generally, samples collected directly at the exit port are those which cannot be detected in the UV region of the electromagnetic spectrum or by a change in refractive index. Brine fractions, for example, are collected for subsequent analysis by atomic absorption spectroscopy (AA), inductively coupled plasma emission spectroscopy (ICP/AES), or for gas chromatographic analysis (GC).

To duplicate the linear flow rates found in subsurface waste injection systems, the high-pressure pumping system must provide a constant flow rate, 1 ft/day (0.3 m/day) or greater, with negligible pulsation at operating pressures approaching 3,675 psi (25.3 MPa). The pump must have an inlet manifold capable of switching from one fluid to another without disruption or mixing of the flow regime. This is accomplished by assuring that the connections of the inlet manifold have zero dead volume. A Waters HPLC pump capable of 6,000 psi (41.4 MPa) pressure and reservoir flow rates was used for these tests.

The pressure applied to the outside of the core contained in the rubber sleeve simulates the overburden pressure on an aquifer system and prevents leakage of the fluids pumped through the core as the internal pressure of the system is increased. The core is isolated by means of an inert Teflon wrapping, as shown in figure 2. The core size used is 1.5 in. (3.81 cm) in diameter by 4 to 6 in. (10.16 to 15.24 cm) in length.

The overburden pressure is simulated using a standard hydraulic pump with a pressure capability of at least 5,000 psi (34.5 MPa). Control valves (Fig. 1) provide for release of pressure that is generated as the core sample is being brought up to operating temperature.

The flow lines shown in figure 2 are assembled using stainless steel tubing. The tubing connections are made with 316 stainless steel Swagelok fittings. This design permits the analysis of reactive materials such as brine solutions and corrosive chemical compounds. Capillary tubing is used where possible to minimize dead volume. The total internal volume of the system shown is 3.86 milliliters.

The stainless steel test cell is shown in figure 3. The cell, machined from 321 stainless steel tubing stock with an inside diameter of 2.5 inches and an outside diameter of 3.0 inches, has been tested to a pressure of 10,000 psi (68.9 MPa), which is more than twice the normal operating pressure.

Core Samples

A Frio core was obtained from the Copano St. 104-7 well, West Fulton Beach field, Aransas County, Texas. The Frio formation is Oligocene-Miocene Age and has produced about 6 billion barrels of oil and 60 trillion cubic feet of gas.

The Frio core sample used in the experiments came from the interval between the subsurface depths of 7,154 to 7,155 feet. The porosity of the sample was 36 percent, and the permeability was 1.7 Darcies. The sample was analyzed by x-ray diffraction, and table 1 indicates the composition found.

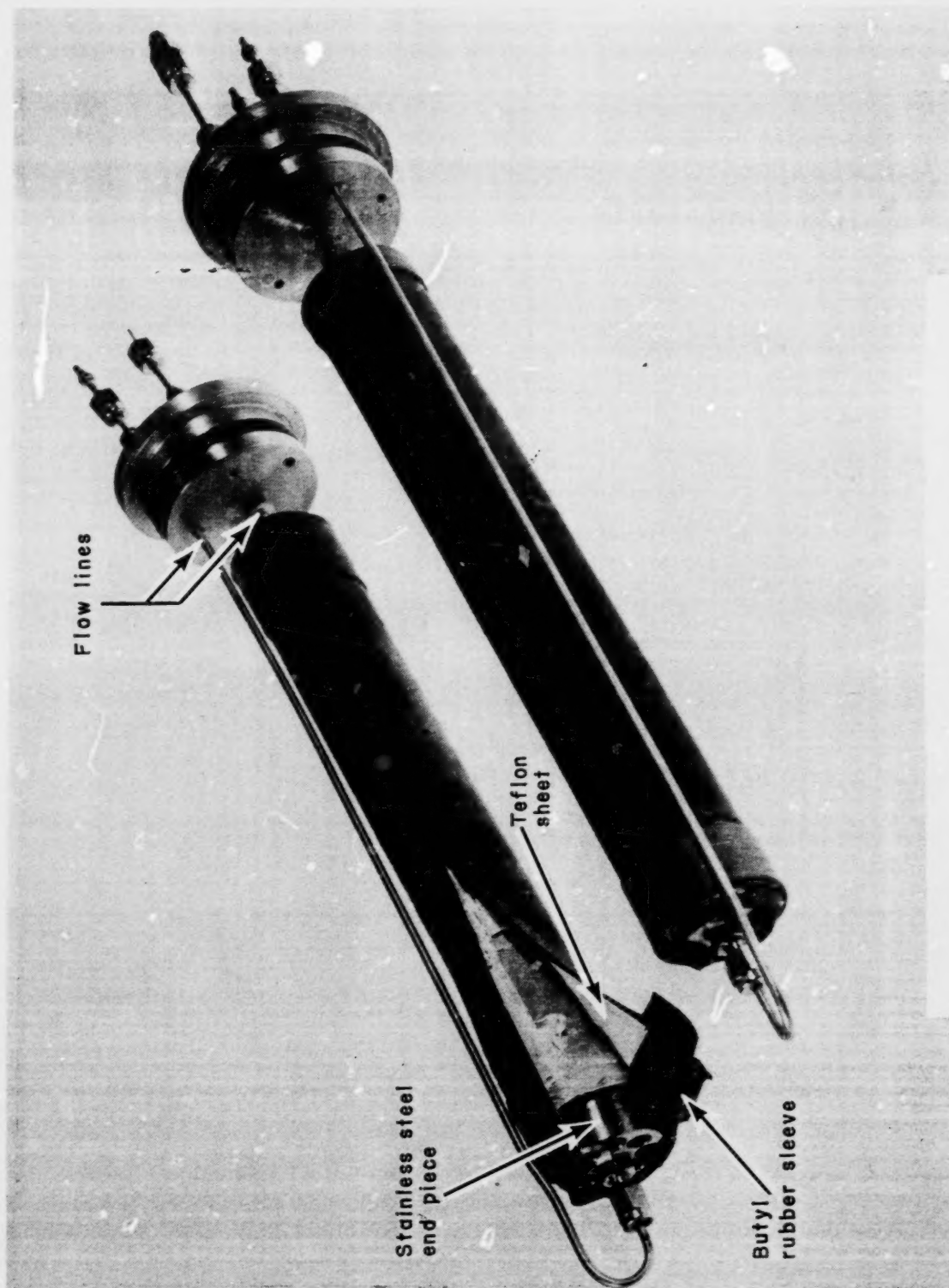


FIGURE 2. - Detail of core mounting assembly.

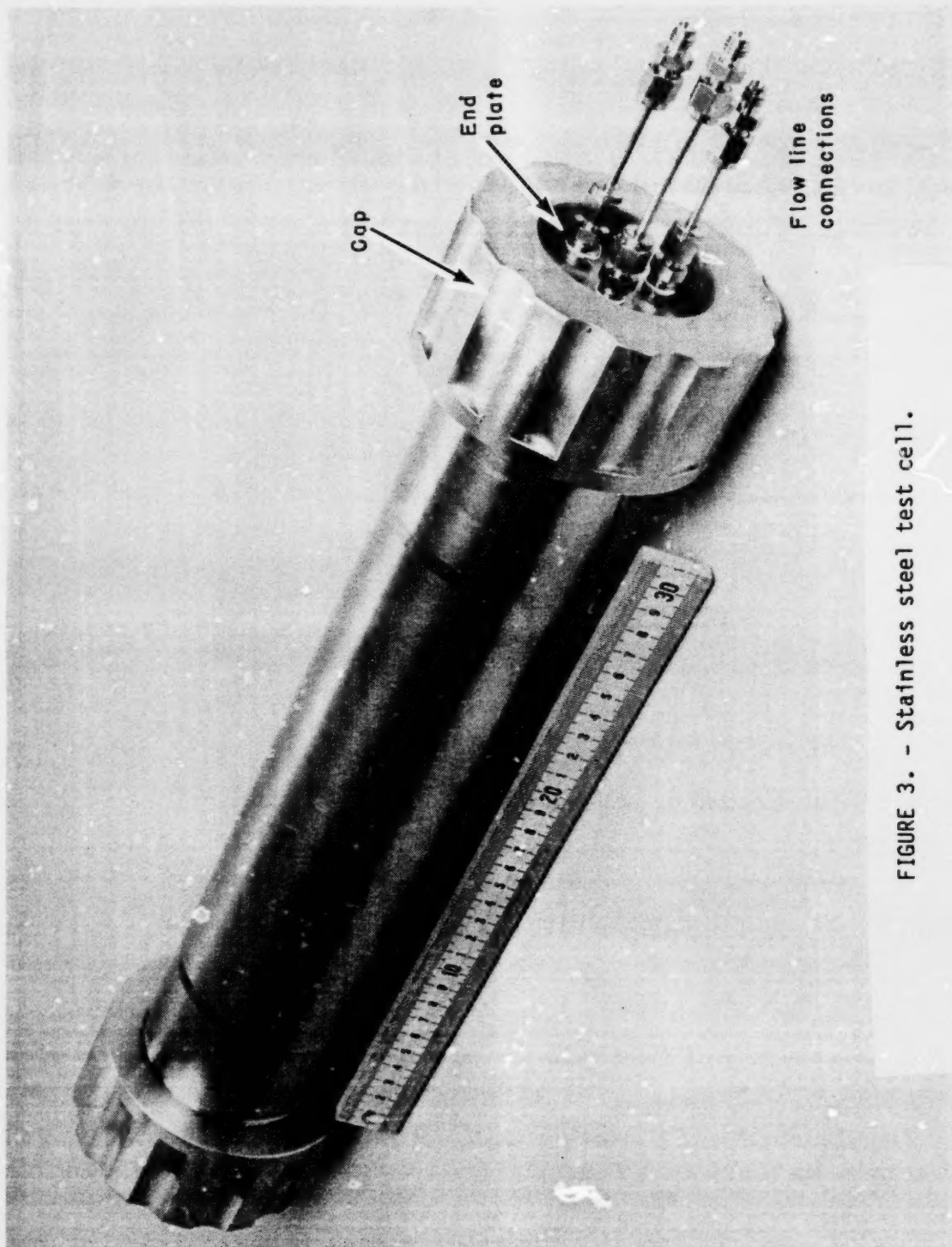


FIGURE 3. - Stainless steel test cell.

TABLE 1. - X-ray diffraction analysis of the Frio rock

Mineral	Weight Percent
Quartz	52.0
Feldspar	17.0
Calcite	28.0
Pyrite	Trace
Kaolinite	3.0
Illite	Trace

Some data are presented in this report that NIPER obtained in laboratory experiments using Cottage Grove rock. The Cottage Grove formation is representative of some sandstone formations into which waste solutions are injected for disposal.

The porosity of the Cottage Grove sandstone is 26 percent, and the permeability is 284 millidarcies. Table 2 shows the results of an x-ray diffraction analysis of the Cottage Grove sandstone.

TABLE 2. - X-ray diffraction analysis of the Cottage Grove rock

Mineral	Weight Percent
SiO ₂	75.4
Al ₂ O ₃	5.8
K ₂ O	5.7
Kaolinite	6.0
Chlorite	1.0
Illite/mica	6.0

Core Preparation

Detailed procedures used for core preparation and determination of brine porosity of the core are described in appendix B.

Hazardous Wastes

As previously noted, phenol and 1,2-dichloroethane were selected as the organic hazardous wastes to study in the Frio formation. Table 3 lists the organic compounds and their pertinent physical properties and the concentration ranges that were used in this study. The low-concentration ranges were selected after a series of tests were run with a gas liquid chromatograph to determine the lower limits of detectability using

TABLE 3. - Organic compounds used in the equilibrium adsorption experiments and the concentration range used for each compound

Compound	Density, g/ml	Boiling point, ° C	Solubility in water, g/100 ml	Concentration range, mg/l
1,2-Dichloroethane	1.257	83.5	0.87 at 20° C	500 - 5,000
Phenol	1.072	182	6.7 at 16° C	500 - 10,000

a hydrogen flame ionization detector; 10,000 ppm was selected for the high concentration because the analysis of numerous aqueous industrial wastes indicates that any single organic component in wastes treated for underground disposal is usually less than 1.0 percent. Sometimes the high concentration was limited by the solubility of the compounds in the dilute sodium chloride brine, which was used as the diluent in all tests.

Frio Brine System

The connate brines found in the Frio formation vary in composition. The salinity (total dissolved solids) can be as low as 16,000 milligrams per liter (mg/l) in some of the geopressed wells and more than 100,000 mg/l in normally pressured wells. The dominant ions are sodium and chloride; however, the usual gamut of alkali, alkaline earth, and halide ions plus trace elements are present. A dilute sodium chloride solution was used in our initial development and demonstration verification experiments.

Experimental Brine and Waste System

Reagent grade chemicals were used in all of the experimental work. The sodium chloride solution contained 10.17 grams/liter of sodium chloride diluted with milli-Q water. Stock solutions of the phenol and 1,2-dichloroethane were made to the exact milligrams per liter (mg/l) needed using the sodium chloride solution as the diluent.

Fluid Flow System Operation

Dynamic flow experiments were performed using 500, 5,000, and 10,000 ppm phenol solutions. The following experimental conditions were used:

Overburden pressure, psi	3,400-3,500
Internal pressure, psi	2,900-3,000
Pump pressure, psi	2,900
Injection rate, ml/min	0.3
Temperature, °F	100/140

The core was mounted in the cell; the constant rate pump was primed; and a simulated overburden pressure 300 psi (2068 kPa) above internal pressure was applied around the core. The flowing pressure of the system, controlled by the spring setting of the pressure control valve, was set to the desired pressure, and the initial solution was pumped through the core. During this

period, the temperature of the cell was gradually increased to the desired temperature. When the predetermined temperature and pressure settings reached equilibrium, the sample was injected into the core by means of the injection valve; simultaneously, the fraction collector and recorder were activated.

Static System

The Frio core was used as the solid adsorbing phase for the static experiments and the organic wastes used were phenol and 1,2-dichloroethane. The static test systems permitted long-term evaluation of the organic wastes. Consolidated core was crushed and sized to pass a No. 20 mesh sieve (841 microns). A stock solution was made of the selected hazardous waste using the reference brine. Each individual test series consisted of one blank sample plus the experimental samples. Solutions of the hazardous wastes were brought into contact with 1 gram of crushed sand stone, and the unit was sealed. A commercially available Paar bomb was used as the test unit. The units were then placed in an oven at the test temperature selected. The individual samples were evaluated at appropriate intervals with a gas chromatograph and compared to hazardous waste standards. Final evaluations included the analysis of the blank to validate the integrity of the static test.

A second series of static tests was conducted to evaluate adsorption rates for phenol and 1,2-dichloroethane. This test series was essentially the same as that described above. However, in this case, the samples were placed in glass vials and a rock to liquid ratio of 1:1 was used. The samples were shaken during the test period. A series consisted of samples that were collected at 2-, 4-, 6-, and 24-hours for analysis by gas chromatography. The amount of adsorption was determined by comparing the hourly samples to the initial test concentration.

Fluids Tested

The fluids tested consisted of a solution containing 10.17 grams of sodium chloride per liter plus the phenol or 1,2-dichloroethane. Phenol concentrations of 500, 5,000, and 10,000 mg/l were added to the sodium chloride stock solution for both the static and flow-through experiments. The amounts of 1,2-dichloroethane added to another series of sodium chloride stock solution were 500, 2,500 and 5,000 mg/l for the static experiments.

The pH of the flow-through solutions before reaction with the Frio rock was 5.7, while the pH of the solutions after reaction with the Frio rock was 8.1. These pH changes indicated that the solutions probably were reacting with the minerals in the rock such as calcite. Table 4 shows an analysis for calcium, magnesium, and sodium of an input and output (after reaction with the Frio rock) phenol solution.

The data in table 4 indicate that sodium decreased in concentration in the effluent phenol solutions at both reaction temperatures of 100° and 140° F., while calcium and magnesium concentrations increased. Because sodium decreased while calcium increased in solution, the probable reaction mechanisms are ion exchange and calcite dissolution.

TABLE 4. - Atomic absorption analysis of an input phenol solution and an effluent phenol solution

	Calcium, mg/l	Magnesium, mg/l	Sodium, mg/l
Input Phenol Solution	0.0	0.0	4,750
Effluent Phenol 10,000 mg/l 100°F	363	0.50	2,200
Effluent Phenol 10,000 mg/l 140°F	270	0.50	2,300

Results and Discussion

The following experimental results, although not entirely definitive because of the amount of time required for the experimental design and set-up, are an adequate test of the protocol and are indicative of the results expected from exhaustive testing. The results of this experimental work were compared to previous work involving the evaluation of organic wastes at simulated reservoir temperature and pressure.⁶ Correlations between the two separate experiments were found to be favorable, further corroborating the viability of the protocol.

The end point of the flow-through method was obtained when the effluent was equal to the initial concentration injected into the core. At this point, the system was assumed to be in equilibrium.

The bulk effluent was compared to the original solution injected into the core. This result was on a $\mu\text{g/ml}$ basis. The differences between these amounts were considered adsorption and were calibrated using a range of standards for each concentration tested. The total amount of adsorption for each concentration was determined in micrograms. The adsorbed concentration ($\mu\text{g/g}$) is plotted versus time to obtain equilibrium amounts absorbed at a specific saturation (figures 4 and 5). The total adsorption (micrograms) was divided by the total mass of the core. This yielded adsorption on a $\mu\text{g/g}$ basis. Results of the adsorption/desorption series for phenol at 100° and 140° F are presented in table 5.

The equilibrium amounts adsorbed were then plotted on log-log paper versus the concentration in equilibrium with the rock surface to obtain the Freundlich isotherms as shown in figure 6. The plot was fitted using a linear regression. The experimental measurements made in this work were based on the changes of the solute concentration as a result of adsorption. The measurements represent a displacement of the solvent from an active site with simultaneous adsorption of the solute; hence, an exchange mechanism takes place at the site of adsorption.

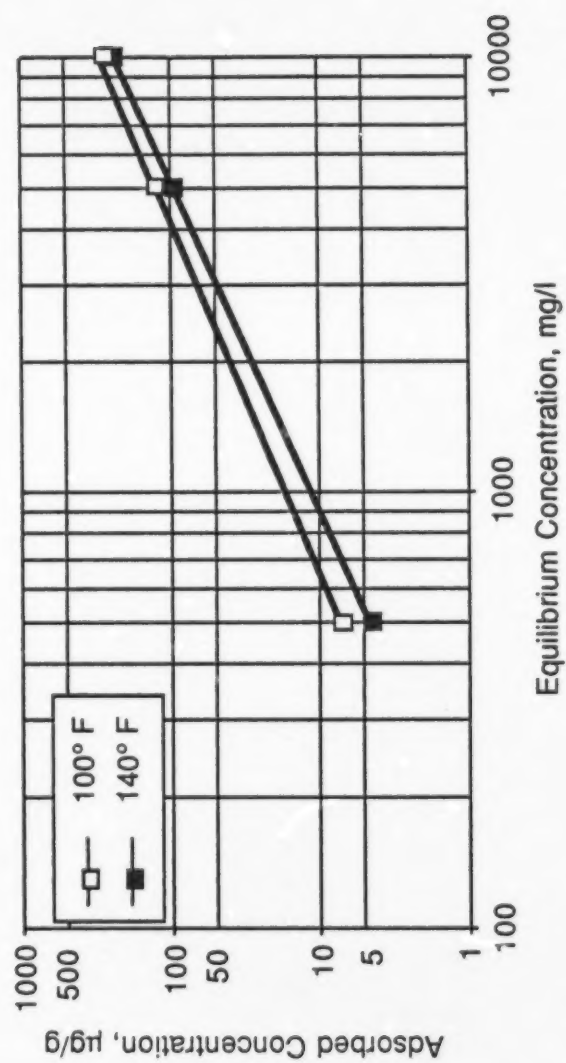


FIGURE 4. - Freundlich isotherm for phenol adsorbed on Frio core.

TABLE 5. - Analytic results for flow-through method using phenol

Compound	Initial concentration mg/l	Temperature, °F	Micrograms adsorbed/ gram of rock	Micrograms Desorbed/gram of rock
Phenol	500	100	9	0
	5,000	100	76	0
	10,000	100	312	0
Phenol	500	140	5	0
	5,000	140	55	0
	10,000	140	276	0

Previous experiments conducted at NIPER, using a Cottage Grove sandstone core, yielded rates of adsorption for 1,2-dichloroethane and phenol, as shown in figure 5. Figures 6 and 7 show the Freundlich isotherms that were obtained for 1,2-dichloroethane and phenol using a Cottage Grove sandstone core.⁶ The technique used is described in reference 6.

Static adsorption curves obtained by plotting the amount of hazardous organic waste adsorbed as a function of time for two compounds are presented in figures 8 and 9 for the Frio sandstone core samples and in figure 5 for the Cottage Grove sandstone core. All of the curves are similar in shape, exhibiting a rapid initial rate of adsorption which declined to zero as equilibrium was approached. By assuming that the rate of adsorption is proportional to the proximity of the system to equilibrium, a rate constant for the adsorption may be calculated from the expression:

$$\frac{dC}{dt} = k(C_{\infty} - C_1) , \quad (1)$$

which reduces to:

$$k = \frac{1}{t} \ln \left(\frac{C_{\infty}}{C_{\infty} - C_1} \right) . \quad (2)$$

The rate constants for each sample are listed in table 6. The rate constants were valid for 75 to 80 percent of the total adsorption rate curve. At that point, the rate constant decreased, indicating that the relationship could no longer be expressed by a simple mechanism.

The rate constants showed a consistently slow rate of adsorption for compounds and were numerically close. Two anticipated results are obvious from table 6: (1) An increase in temperature caused a decrease in the rate constants for the compounds, and (2) an increase in concentration produced an increase in the rate constants. Rate constants can be obtained using the flow-through method. The results can be obtained by sampling the effluent from the flow-through method at specified time intervals for each concentration level analyzed. After the samples are analyzed by GLC for specific concentration, the concentrations are then plotted as a function of time.

Smith⁷ breaks the overall process of adsorption into several physical processes that represent the sequence of events taking place when a molecule is transferred from a solution to an active adsorption site on a solid

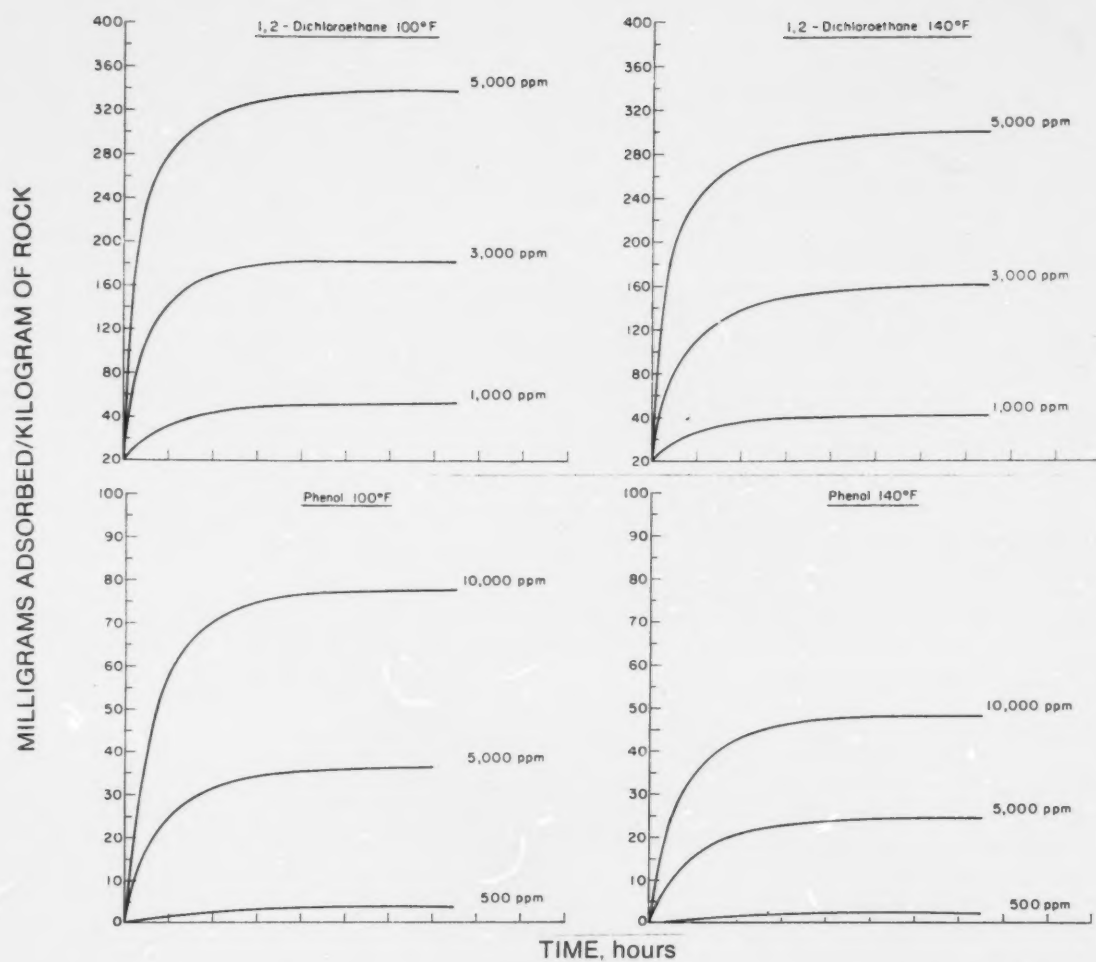


FIGURE 5. - Rates of adsorption of 1,2-Dichloroethane and phenol on Cottage Grove sandstone.

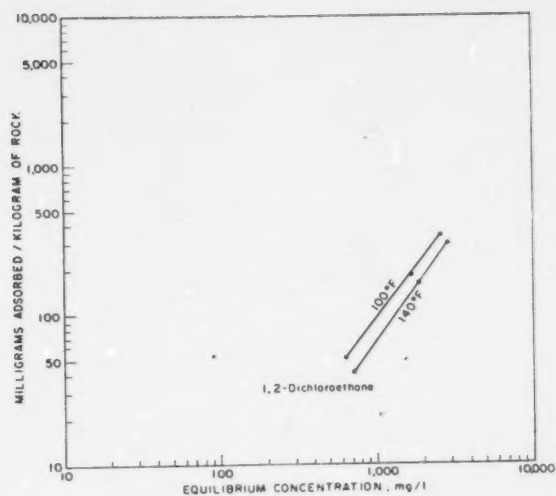


FIGURE 6. - Freundlich isotherms of 1,2-dichloroethane on Cottage Grove sandstone.

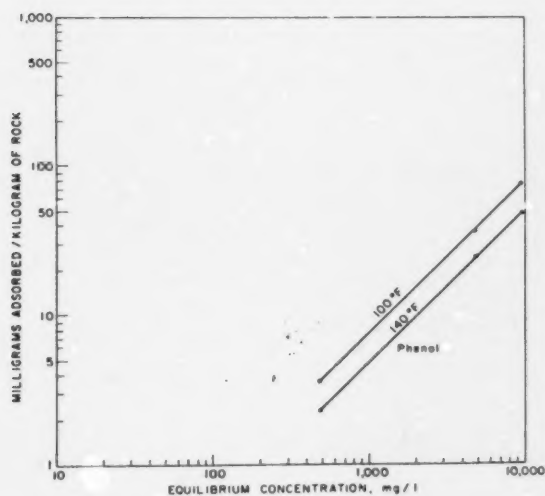


FIGURE 7. - Freundlich isotherms of phenol on Cottage Grove sandstone.

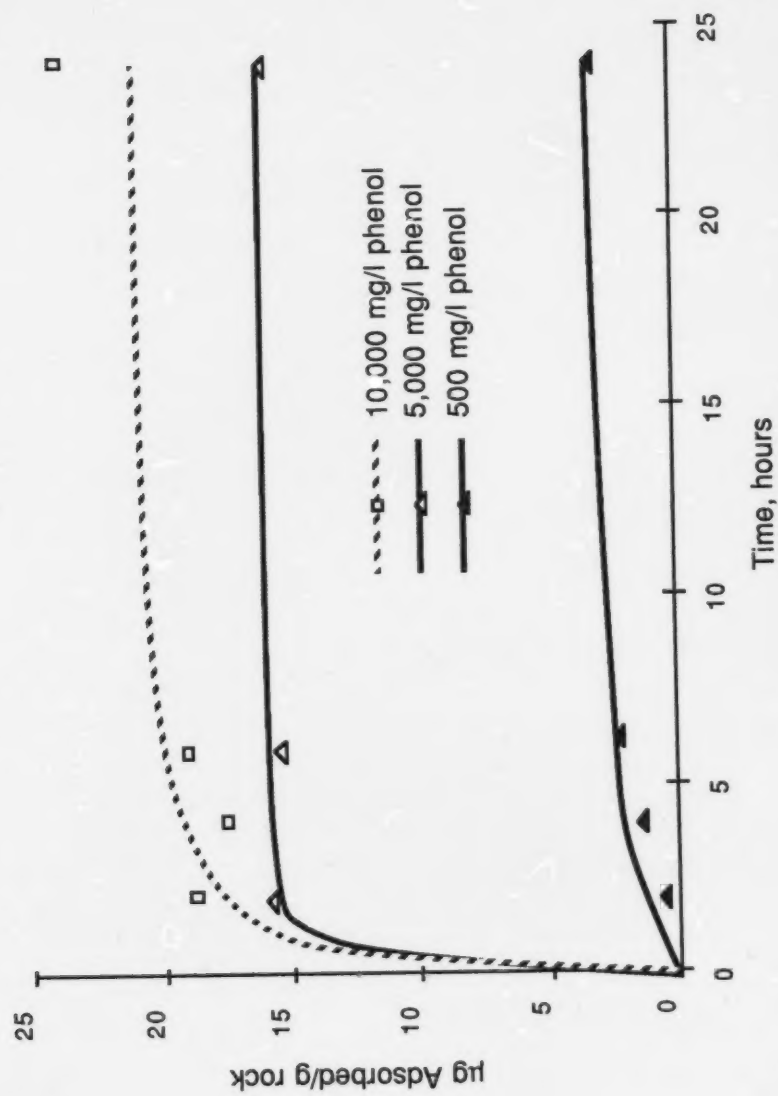


FIGURE 8. - Rates of adsorption of phenol at 100° F using a Frio core.

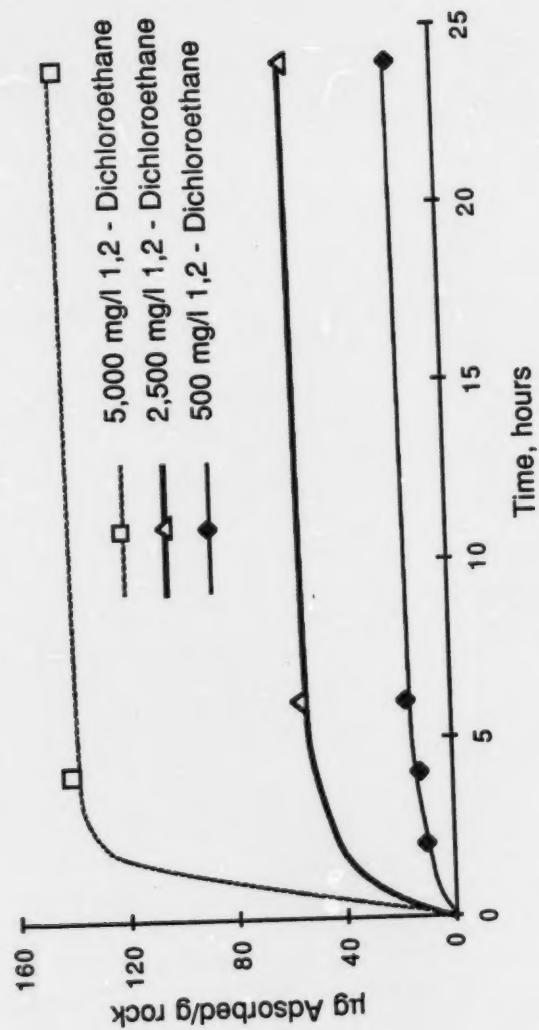


FIGURE 9. - Rates of adsorption of 1,2-Dichloroethane at 100° F using a Frio core.

TABLE 6. - Rate constants for each compound tested at specific initial concentrations and temperatures

Compound	Initial concentrations, ppm	k, 1/hour	Temp, °F	k, 1/hour	Temp, °F
1,2-Dichloroethane ¹	1,000	0.091	100	0.086	140
	3,000	0.066	100	0.116	140
	5,000	0.169	100	0.159	140
1,2-Dichloroethane ²	500	0.48	100	(³)	(³)
	2,500	0.61	100	(³)	(³)
	5,000	0.98	100	(³)	(³)
Phenol ¹	500	0.060	100	0.055	140
	5,000	0.115	100	0.098	140
	10,000	0.130	100	0.122	140
Phenol ²	500	0.25	100	(³)	(³)
	5,000	0.73	100	(³)	(³)
	10,000	0.87	100	(³)	(³)

¹ Cottage Grove sandstone. ² Frio sandstone. ³ Not determined.

surface. These steps are: (1) transfer from the bulk phase to the proximity of the surface by molecular or convective diffusion; (2) diffusion into the pores to the sites of adsorption; (3) finally, adsorption onto the site; and (4) where chemical reaction takes place, steps 2 and 3 occur in reverse for a product.

Chemical reaction is not involved in the adsorption process for the organic compounds presented in this report; thus, step 4 is not applicable. The rate at which adsorption on the site takes place (step 3) for aqueous solutions is very rapid, especially when accompanied by a loose bond which is indicated by a low heat of adsorption. The heats of adsorption calculated for the compounds were all less than 8 k-cal/g-mole indicating weak Van der Waal type physical adsorption in all cases. Therefore, owing to the high rate of adsorption involved in step 3, this step does not influence the overall kinetics of the adsorption process. This leaves bulk and internal pore diffusion (steps 1 and 2) as the steps controlling the adsorption kinetics. Since diffusion is the controlling mechanism, it is not unusual for all of the compounds to exhibit adsorption rate constants that are numerically close. This leads to the conclusion that the molecular diffusivities in water of all of the compounds tested are equivalent in value. To test this, the diffusivities of the compounds were calculated (table 7) for each temperature by use of the equation developed by Wilke and Chang.⁸ Since the calculated diffusivities are equivalent, they provided added verification that the rate process is diffusion-controlled.

Freundlich-type isotherms (figures 6, 8-9) expressed by equation 3 fit the equilibrium experimental data.

$$A_1 = FC_1^n \quad (3)$$

Consideration of the intercept, F , and the slope, n , of the Freundlich isotherms provides some quantitative information about the nature of the adsorption.

The relationships of F to the free energy changes that occur in the adsorption process are discussed by Haque and Coshaw⁹ and Crisp.¹⁰ The surface site equilibrium is represented by equation 4:

$$(C_1) \rightleftharpoons (C_s) \quad (4)$$

where C_1 and C_s represent the activity of the component in the solution and adsorbed on the surface for dilute solutions.

TABLE 7. - Calculated values of the coefficients of molecular diffusion for each compound in water at the temperature of interest

Compound	D, cm ² /hr	Temp, °F	D, cm ² /hr	Temp, °F
1,2-Dichloroethane	0.0529	100	0.0846	140
Phenol	.0479	100	.0763	140

Equation 4 may be represented by equation 5 where K_e is the overall equilibrium constant:

$$K_e = \frac{(C_s)}{(C_1)} \quad (5)$$

Equation 5 is a special case of the Freundlich isotherm where n is equal to unity.⁹ Furthermore, it was shown that for adsorption of two herbicides from aqueous solutions onto clays, K_e of equation 5 approaches the Freundlich isotherm intercept constant, F .⁹ With the exception of 1,2-dichloroethane, the compounds tested for this work and the Cottage Grove work⁶ have values of n which are very close to unity. Hence, the intercept, $\log F$, provides an indirect measurement of the surface-free energy change, namely:

$$\Delta G = RT \ln F \quad (6)$$

The Freundlich isotherm constants for phenol in the Frio sandstone experiments and for 1,2-dichloroethane, and phenol in the Cottage Grove sandstone experiments at each temperature are listed in table 8. In all cases, as the temperature increased the numerical value of F decreased which is characteristic of the exothermic nature of adsorption.

The adsorption experiments were conducted at two temperatures in order to calculate the isosteric heats of adsorption which are indicative of the nature of the surface bonding. The isosteric heat of adsorption is defined as the enthalpy difference between 1 mole of adsorbent at any activity and 1 mole of adsorbate in equilibrium with the adsorbent. Thus:

$$\Delta H_{iso} = H^0_s - H^0 = -R \frac{d[\ln(C_s/(C_1))]}{d(1/T)} \quad (7)$$

The isosteric heat of adsorption is obtained by measuring the equilibrium amount of the compound that is adsorbed at two temperatures from dilute solutions and solution of equation 7. The heats of adsorption obtained in this manner are listed in table 9. All of the values are less than 8 k-cal/gmole; hence, the most probable mechanism of the adsorption is Van der Waal-type bonding, or physical adsorption.

TABLE 8. - Constants F and n for the Freundlich isotherms shown in figures 4, 6-7

Compound	Temperature, °F	Freundlich constants	
		$F(k)$	n
1,2-Dichloroethane ¹	100	0.010	1.33
	140	.003	1.43
Phenol ¹	100	.007	1.01
	140	.004	1.01
Phenol ²	100	.003	0.81
	140	.001	0.76

¹ Cottage Grove sandstone. ² Frio sandstone.

TABLE 9. - Isosteric heats of adsorption calculated for each concentration of the compounds that were tested

Compound	Concentration, mg/l	-ΔH, k-cal/g-mole
1,2-Dichloroethane ¹	1,000	3.25
	3,000	1.97
	5,000	2.00
Phenol ²	500	4.19
	5,000	2.45
	10,000	1.84
Phenol ¹	500	4.22
	5,000	3.63
	10,000	4.21

¹ Cottage Grove sandstone. ² Frio sandstone.

DESORPTION AND DEGRADATION EXPERIMENTS

Subsequent to the adsorption experiments with the dynamic fluid flow-through core experiments, brine containing no phenol was flushed through the core. Analysis of the effluents produced indicated no desorption of the phenol. Effluents generated in the dynamic fluid flow experiments were analyzed for degradation products, but none were found.

Static tests also were performed using crushed Frio rock in the presence of brine and phenol on a sealed system at 140° F for 83 days. Phenol adsorption onto the rock occurred in the amount of 40 μg of phenol per gram of rock. No phenol degradation products were detected in the liquid phase.

OBSERVATIONS

The experimental results obtained were evaluated by comparison with some previous experiments which were performed at NIPER⁶. This comparison permitted a method of corroboration of the developed protocol in lieu of more time consuming testing of the new flow-through method. Time did not permit collection of sufficient data to establish firm precision and bias statements for the newly developed methods; however, the comparisons with previous experiments⁶ indicate that the flow-through method is viable and that it can be applied to evaluate additional subsurface reservoir rocks and hazardous organic wastes. Evaluation and comparison of the results indicate several premises:

1. The rate of adsorption of the organic waste compounds is proportional to their concentration in solution and inversely proportional to the temperature.
2. The adsorption process was exothermic for phenol and 1,2-dichloroethane.

3. The numerical values for the isosteric heats of adsorption were less than 8 k-calories per gram mole for phenol and 1,2-dichloroethane indicating that Van der Waal, or physical adsorption occurred.

RECOMMENDATIONS FOR FUTURE USE OF PROTOCOL

The protocol was designed for application in evaluating mobility, adsorption, and degradation of hazardous organic chemicals in a simulated deep subsurface environment. The following section outlines the developed laboratory procedures.

Core Analysis

The core consists of an appropriate sample of the subsurface reservoir rock, which can be obtained by using a core sampling device while drilling a deep well¹¹ or from an outcrop of the appropriate rock formation.⁶ The core is analyzed for organic and inorganic constituents and minerals of interest by application of procedures in appendix B in the Core and Brine Evaluation section.

Next, an appropriate sample of the core is prepared and analyzed for brine porosity and permeability as described in appendix B in the Core Preparation section. The usual core size is 1.5 in. (3.81 cm) in diameter by 4 to 6 in. (10.16 cm to 15.24 cm) long. The dispersion experiments are performed as described in appendix B to assure that the assembled system is an integral unit and does not contain channels, bypass or other inconsistencies.

Organic Hazardous Waste and Brine Analysis

The organic hazardous wastes usually are mixed with an aqueous brine solution prior to their injection into a deep subsurface reservoir. The amount of organic hazardous waste that can be thus mixed is dependent upon its solubility in the aqueous brine, and information such as that shown in Table 3 should be determined.

Appropriate organic hazardous waste and brine mixtures are prepared and analyzed using the desired procedures as described in appendix B in the Core and Brine Evaluation section and the Analysis of Phenols and Phenol Degradation By-Products section. The procedures referenced in the Analysis of Phenols and Phenol Degradation By-Products section include standard methods for numerous organic compounds.

Determination of Adsorption-Fluid Flow Method

Mount the core in the fluid flow test cell apparatus as shown in figure 1, and introduce the test fluids through the core as described in the sections on Dynamic Fluid Flow System and Fluid Flow System Operation. Analyze effluent samples periodically to determine when the concentration of the organic hazardous waste is equal to the concentration of the injected fluid, this is the end point or the equilibrium point.

Use the total mass of the core and calculate the adsorption in $\mu\text{g/g}$ as illustrated in table 5. Plot the equilibrium amounts adsorbed versus the concentration in equilibrium with the rock surface to obtain the Freundlich

isotherms as shown in figure 4. A rate constant can be calculated by using equation 2. The coefficients of molecular diffusion can be calculated (table 7) to determine if diffusion is the controlling mechanism.

The constants, F and n , can be calculated as shown in table 8 to determine the probable nature of adsorption. The isosteric heats of adsorption can be calculated (table 9) using equation 7 to determine the probable mechanism of adsorption.

Desorption experiments may be performed by injecting or pumping brine solutions containing no organic hazardous waste compound through the core and analyzing the effluents produced for the compounds that were previously adsorbed.

Determination of Adsorption-Static Method

The static method can be used, not only for determining the degree of adsorption, but also for evaluation of core dimension and adsorption potential for the flow-through method. Using the static method, the crushed core material is introduced into vials and the hazardous waste is brought into contact with the core material. Each individual test series consists of a blank plus the samples to be tested. The test series consists of a 2-, 4-, 6-, and 24-hour set. The units are placed in a shaker bath at the appropriate temperature. At the selected time, samples are collected and the adsorption is evaluated using a gas chromatograph. The results are compared to standards made from the appropriate hazardous waste. Final evaluations include the analysis of a blank to validate the integrity of the static test procedure. Determination of the level of desorption for the hazardous waste is difficult using the static test due to the unconsolidated nature of the core sample.

Degradation of the sample due to the flow-through method and static method is observed during the normal sample evaluation of the hazardous wastes. If changes are noted in the spectra for the hazardous wastes, appropriate chemicals should be utilized for comparative purposes or the sample should be evaluated using GC/MS for a more quantitative identification.

CONCLUSIONS

The following conclusions are supported by the research described in this manuscript.

1. A protocol was developed whereby organic hazardous wastes can be evaluated for mobility, adsorption, and degradation potentials under simulated subsurface reservoir temperatures and pressures.
2. Long-term (months, not years) evaluations of the organic hazardous waste phenol did not indicate the formation of degradation products.
3. The results obtained with the developed protocol correlated with some previous work performed at NIPER, thus providing a means of corroboration.

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APPENDIX A. - CLASSIFICATION OF INJECTION WELLS
(Source: Code of Federal Regulations, Title 40, Part 146.03)

Injection wells are classified as follows:

a) **Class I.**

- 1) Wells used by generators of hazardous wastes or owners or operators of hazardous waste management facilities to inject hazardous waste beneath the lower most formation containing, within 402 meters (1/4 mile) of the well bore, an underground source of drinking water.
- 2) Other industrial and municipal disposal wells which inject fluids beneath the lowermost formation containing, within 402 meters (1/4 mile) of the well bore, an underground source of drinking water.

b) **Class II. Wells which inject fluids:**

- 1) Which are brought to the surface in connection with conventional oil or natural gas production; and may be commingled with waste waters from gas plants which are an integral part of production operations, unless those waters are classified as a hazardous waste at the time of injection;
- 2) For enhanced recovery of oil or natural gas; and
- 3) For storage of hydrocarbons which are liquid at standard temperature and pressure.

c) **Class III. Wells which inject for extraction of minerals, including:**

- 1) Mining of sulfur by the Frasch process;
- 2) In situ production of uranium or other metals. This category includes only in-situ production from ore bodies which have not been conventionally mined. Solution mining of conventional mines such as stopes leaching is included in Class V
- 3) Solution mining of salts or potash

d) **Class IV.**

- 1) Wells used by generators of hazardous wastes or of radioactive wastes, by owners or operators of hazardous waste management facilities, or by owners or operators of radioactive waste disposal sites to dispose of hazardous wastes or radioactive wastes into or above a formation which within 402 meters (1/4 mile) of the well contains an underground source of drinking water.
- 2) Wells used by generators of hazardous waste or of radioactive waste, by owners or operators of hazardous waste management facilities, or by owners or operators of radioactive waste disposal sites to dispose of hazardous waste or radioactive waste above a formation which within 402 meters (1/4 mile) of the well contains an underground source of drinking water.
- 3) Section 7010 of the Hazardous and Solid Waste Amendments of 1984, bans the use of Class IV wells.

e) **Class V. Injection wells not included in Class I, II, III or IV.**

Class V wells includes:

- 1) Air conditioning return flow wells used to return to the supply aquifer the water used for heating or cooling in a heat pump;
- 2) Cesspools, including multiple dwelling, community or regional cesspools, or other devices that receive wastes, which have an open bottom and sometimes have perforated sides. The UIC requirements do not apply to single family residential cesspools or to non-residential cesspools which receive solely sanitary wastes and have the capacity to serve fewer than 20 persons a day;
- 3) Cooling water return flow wells used to inject water previously used for cooling;
- 4) Drainage wells used to drain surface fluid, primarily storm runoff, into a subsurface formation;
- 5) Dry wells used for the injection of wastes into a subsurface formation;
- 6) Recharge wells used to replenish the water in an aquifer;
- 7) Salt water intrusion barrier wells used to inject water into a fresh water aquifer to prevent the intrusion of salt water into the fresh water;
- 8) Sand backfill and other backfill wells used to inject a mixture of water and sand, mill tailings or other solids into mined out portions of subsurface mines whether what is injected is a radioactive waste or not;
- 9) Septic system wells used to inject the waste or effluent from a multiple dwelling, business establishment, community or regional business establishment septic tank. The UIC requirements do not apply to single family residential septic system wells, or to non-residential septic system wells which are used solely for the disposal of sanitary waste and have the capacity to serve fewer than 20 persons a day.
- 10) Subsidence control wells (not used for the purpose of oil or natural gas production) used to inject fluids into a non-oil or gas producing zone to reduce or eliminate subsidence associated with the overdraft of fresh water;
- 11) Radioactive waste disposal wells other than Class IV;
- 12) Injection wells associated with the recovery of geothermal energy for heating, aquaculture or production of electric power;
- 13) Wells used for solution mining of conventional mines such as stopes leaching;
- 14) Wells used to inject spent brine into the same formation from which it was withdrawn after extraction of halogens or their salts; and
- 15) Injection wells used in experimental technologies.

APPENDIX B. - EXPERIMENTAL PROCEDURES

- I. Core Preparation
- II. Core and Brine Evaluation
- III. Analyses of Phenols and Phenol Degradation By-Products

I. Core Preparation

Many of the procedures used in the core preparation are referenced in "*Properties of Reservoir Rocks: Core Analysis*" by Monicard.¹¹

Determine Brine Porosity of a Consolidated Core

The procedure for the determination of porosity is as follows:

1. Determine dimensions of core.
2. Mount the core in the rubber sleeve along with end caps and fittings with a known dead volume (volume of fluid occupied by fittings), as shown in figure B-1.
3. Determine the dry weight of the core, rubber sleeve, end caps, and fittings, see figure B-1.
4. Saturate core with brine solution.
5. Determine saturated core weight.
6. Determine weight and volume of brine reservoir.
7. Calculate porosity and pore volume.

Details of each of these seven steps are as follows:

1. Core Dimensions

Measure three diameters 120° apart on each end of the clean dry core in inches and/or centimeters. Measure the length of the core at four equally spaced positions around the circumference.

Record the measurements and compute the average length and diameter in centimeters and/or inches. Weigh the core and record it as w .

2. Mount Core in Rubber Sleeve

(a) The rubber sleeve is mounted on the core using a Hassler core holder fitted with end caps, as shown in figure B-1. The advantage of using Delrin material for end caps is its light weight and resistance to chemicals. Ensure that the end caps fit tightly against the core leaving no gap between end cap and core.

(b) Pass CO_2 through the core at 30-70 psi for 30 minutes (depending on the length of the core) to displace air.

3. Determine Dry Core Weight

(a) Disconnect tubing (Fig. B-1) and remove rubber sleeve, end caps, and core from the Hassler core holder.

(b) Weigh the core with rubber sleeve, tubing, and end caps and record it as w_1 .

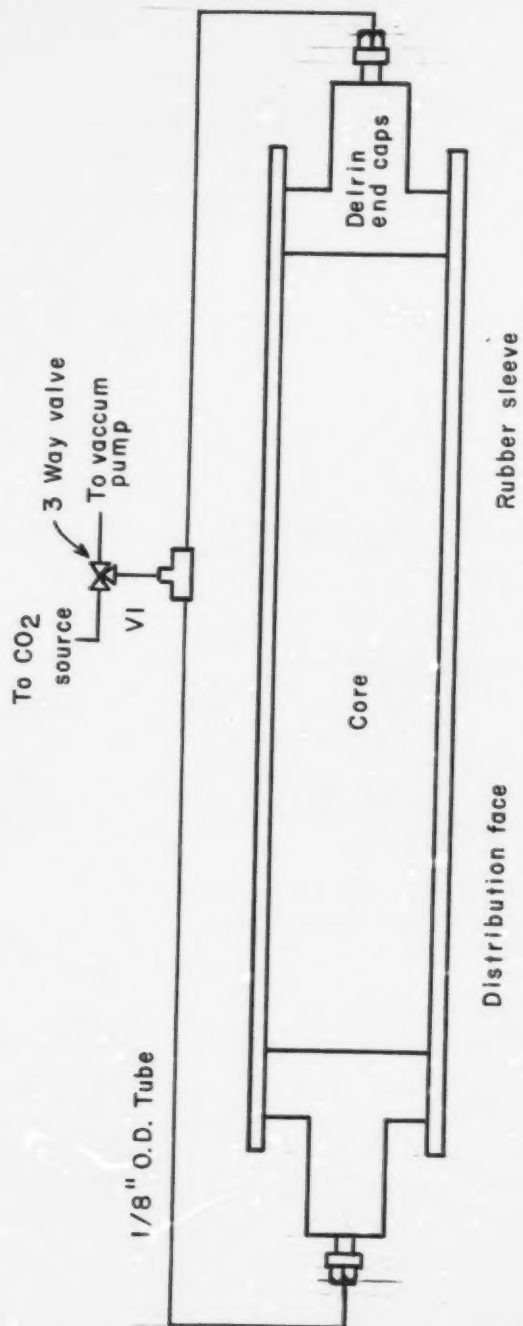


FIGURE B-1. - Schematic diagram of core setup.

(c) Mount the core back on the Hassler core holder and increase the confining pressure to 200 psi by means of a hydraulic pump and through valve V2.

(d) Deaerate the brine in the brine reservoir (Fig. B-2) by connecting the brine reservoir to the vacuum pump and evacuate for about 3-5 minutes. A vacuum of 2000 microns of mercury is sufficient. With the pump on, close valve V3 (Fig. B-2) to retain the vacuum on the brine reservoir.

(e) Disconnect the CO₂ tubing from valve V1 (Fig. B-1) and turn valve V1 to the vacuum source to evacuate the core making sure that the vacuum pump is on.

(f) Continue evacuating CO₂ from the core until the vacuum gauge reads 250-500 microns of mercury. Do not shut off the vacuum pump.

(g) Open brine reservoir valve V3 (Fig. B-2) and three-way valve V3 (Fig. B-1) to admit brine to core sample and add brine until core sample is completely saturated with brine.

(h) Turn the vacuum pump off and allow the core sample to remain in contact with the brine for 30 minutes to ensure that the core is 100% saturated.

(i) Close valve V3 to the brine reservoir and then disconnect the brine reservoir from the core saturating unit.

4. Determine Saturated Core Weight

Release any confining pressure and remove the core, rubber sleeve, and end caps from the core holder. Weigh the core, rubber sleeve, end caps, and fittings. Record this weight in the laboratory notebook as W_2 .

5. Determine Weight/Volume of Brine Reservoir

The weight of the brine reservoir is measured and recorded as w_3 . The density of the brine, if not known, is measured using a Mettler-Paar densitometer.

6. Calculate Porosity and Pore Volume

The dead volume or the void volume of the tubing, valves, end caps, and distribution face is calculated as V_d (cm³). The quantities measured are listed below:

(a) Core Sample:

Average length of core = L (cm)

Average diameter of core = d (cm)

Bulk volume of core = $L \times (d^2 \div 4) \times 3.1416 = V_B$ (cm³)

Weight of dry clean core = w (gm)

(b) Weight of dry core + rubber sleeve + tubing + valve + end caps
= w_1 (gm)

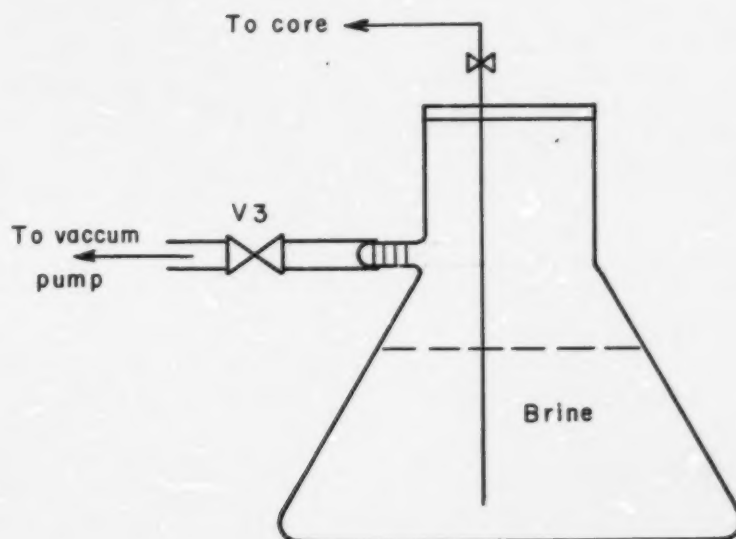


FIGURE B-2. - Schematic diagram of brine reservoir.

(c) Weight of saturated core + rubber sleeve + tubing + valve + end caps
= w_2 (gm)

(d) Change in weight of brine reservoir after saturation = w_3 (gm)

(e) Dead volume of tubing, valves + end caps = V_d (cm³)

Calculations

$$\text{Area of core} = \frac{\pi d^2}{4} = A [\text{cm}^2]$$

$$\text{Bulk volume of core} - L \times A (\text{cm}^3) = V_B (\text{cm}^3)$$

$$\text{Pore volume of core} = \frac{(w_2 - w_1)}{\rho_w} - V_e = PV_1 (\text{cm}^3)$$

$$\text{Pore volume of core} = \frac{(w_3)}{\rho_w} - V_d = PV_2 (\text{cm}^3)$$

$$\% \text{ Difference} = \frac{PV_1 - PV_2}{PV_2} = \text{PDIFF}$$

If PDIFF over 5% recheck w_1 through w_3 .

$$\text{Average pore volume} = \frac{PV_1 + PV_2}{2} = PV (\text{cm}^3)$$

$$\text{Porosity} = \frac{PV}{V_B} \times 100 = \%$$

7. Dispersion Experiments⁷

Dispersion experiments are conducted using brine solutions of different concentrations; that is, a step increase from a low brine concentration to one that is higher. The brine solutions are injected through the core sample at a continuous rate, and the eluting samples are caught in the fraction collector for subsequent analysis.

The brine solutions are prepared with research grade chemicals and water, filtered through a 0.45-micron filter, and degassed for 1 hour to remove entrapped air. The core samples are evacuated to 20 microns of mercury before saturating with the appropriate brine solution. The cores are weighed before and after saturation to obtain the pore volume, which is a requisite for dispersion calculations.

The core sample is mounted in the test cell, as described in the dynamic fluid flow system section; the constant volume pump is primed; and a simulated overburden pressure (300 psi above internal pressure) is applied to the core. The internal pressure of the system, controlled by the spring setting of the pressure relief valve, is set to the desired pressure, and approximately 3 pore volumes of the low concentration brine solution is permitted to flow through the core. During this period, the test cell can be

adjusted to a specified temperature; however, the overburden pressure gauge should be carefully monitored because of the rapid increase in pressure as the temperature rises.

When the desired temperature and pressure reach equilibrium, the high-concentration brine solution is injected by switching the valve at the inlet of the constant volume pump, and, simultaneously, the fraction collector and time versus volume recorder are activated.

The extent of mixing between the injected and displaced fluid in a porous system is conveniently measured by addition of a tracer to the invading fluid and analysis of the effluent tracer concentration as a function of time. In the absence of adsorption, as the fluids move through the porous system, the tracer gradually spreads into the fluid being displaced due to the simultaneous actions of convective and molecular diffusion. Convective dispersion is influenced by the density and viscosity difference between the two miscible fluids and by local variations of the fluid velocity, pore-size distribution, pore constrictions, and the tortuosity of the flow path.

Molecular diffusion can occur by bulk diffusion and by Knudsen diffusion. Wheeler¹² has suggested that Knudsen diffusion must be considered when the mean free path of the diffusing gases is more than 10 times the radius of the pore. He therefore sets a pore radius of 10^{-5} cm as the limit at which bulk diffusion alone will occur and a pore radius of 10^{-6} cm for complete Knudsen diffusion. Knudsen and bulk diffusion occur simultaneously in pores with radii between 10^{-6} and 10^{-4} cm. The pore size distributions measured for five sandstones⁶ show that most of the pores have radii greater than 10^{-4} cm; hence, the contribution from Knudsen diffusion may be considered negligible. Bulk diffusion is concentration dependent and will take place in the absence of fluid flow if a concentration gradient exists between two miscible phases in a porous medium.

Other modes of mass transfer that affect dispersion in porous media are eddy diffusion and transverse molecular diffusion. Laminar flow (45 cm/day) is used in all of the experiments; therefore, eddy diffusion is not a contributing factor to dispersion. Since the ratio of the radius to the length of the sandstone samples used in this work is small (0.075) and the viscosities of the displaced and injected fluid phases are equal, transverse diffusion is neglected. Hassinger and von Rosenberg,¹³ and Grane and Gardner,¹⁴ investigated transverse dispersion in packed columns of spherical beads and presented graphs of the coefficient of transverse dispersion versus the Peclet number.

In this work, variations of density and viscosity between the two miscible phases are eliminated by using aqueous brine solutions. Under these conditions, the coefficient of linear dispersion (D) is a complex function of molecular diffusion, velocity, and tortuosity.

Calculations: When the concentration of tracer entering a system is suddenly increased (the so-called step-function), the response is a direct measure of the residence time distribution of the concentration. If D is zero, there will be no distribution of the effluent concentration with respect to time. This is an ideal limit since any real miscible phase displacement will always have some molecular and convective mass transport across the

boundaries of the two fluids. Hence, the actual tracer response curve is always S-shaped.

The equation applied to the analysis of the effluent tracer-compound concentration curve (response curve) for one-dimensional flow is the diffusivity model (neglecting adsorption).¹⁵⁻¹⁶

$$\frac{\lambda}{L} \frac{\partial^2 C}{\partial \epsilon^2} - \frac{\partial C}{\partial \epsilon} = \frac{\partial C}{\partial \tau} \quad (\text{B-1})$$

$$\lambda = \frac{DA\phi}{Q}; \quad \epsilon = \frac{\phi AX}{V_p} = \frac{X}{L} \quad (\text{B-2})$$

$$\tau = \frac{Qt}{V_p}; \quad C = E_1/C_0 \quad (\text{B-3})$$

For a finite difference solution to equation B-1, the initial and boundary conditions are:

$$C(\epsilon, 0) = 0, \quad 0 \leq \epsilon \leq 1.0 \quad \left[\begin{matrix} X = L \\ \epsilon = 1.0 \end{matrix} \right] \quad (\text{B-4})$$

$$C(0, \tau) = C_0 \frac{\lambda}{L} \frac{\partial C}{\partial \epsilon}, \quad 0 \leq \tau \leq \tau_1 \quad (\text{B-5})$$

$$C(0, \tau) = \frac{\lambda}{L} \frac{\partial C}{\partial \epsilon}, \quad \tau > \tau_1 \quad (\text{B-6})$$

$$C(0, \tau) = 0.0 \quad (\text{B-7})$$

$$\left(\frac{\partial C}{\partial \epsilon} \right)_{\epsilon = 1.0} = 0, \quad \tau > 0 \quad (\text{B-8})$$

The inlet boundary condition for constant ($C_i/C_0 = 1.0$) injection is equation B-5; however, when the input is decreased to zero after a short period of injection (slug injection), the entrance boundary condition becomes equation B-7; hence, the equation for dispersion must be solved with the new boundary conditions after the initial slug input. This is done in the computer program (table B-1), attached at the end of this section, by varying the input datum, VOLIN (volume of tracer injected). If constant concentration injection is used, VOLIN is set equal to PVIMAX (the maximum number of pore volumes for which the program is to run). If slug injection is used, VOLIN is entered as the exact volume of the slug injected. The results of the two modes are shown in figure B-3.

The coefficient of dispersion, DIS, is the only adjustable parameter in the computer program (see table B-1) since the other data are derived directly from the experiment. Hence, the coefficient of dispersion is determined by adjusting DIS in the computer program until the computed curve matches the experimentally determined effluent response curve.

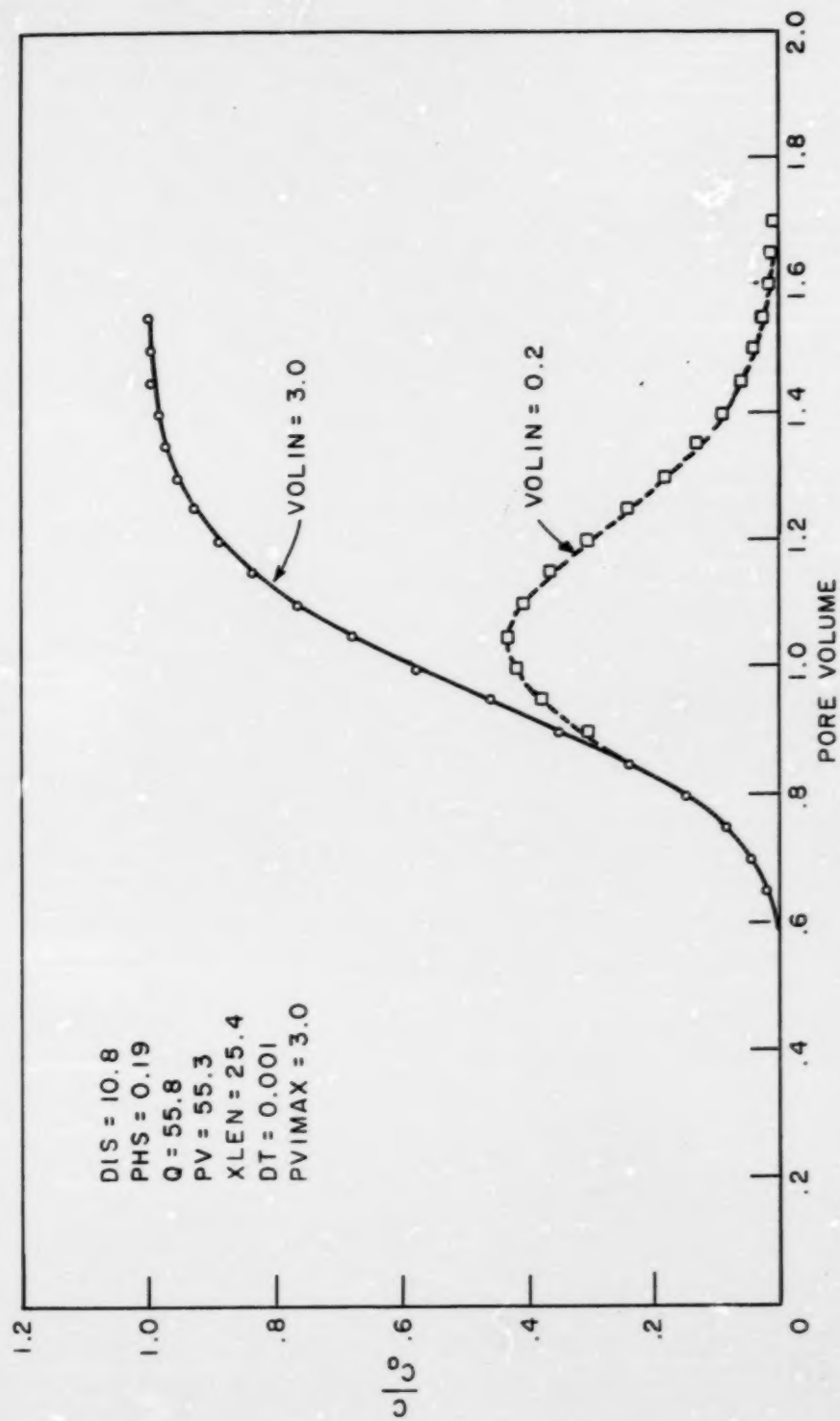


FIGURE B-3. - Computed curves for constant concentration injection and slug injection.

TERMS USED

CHROM	Computer program for determination of chromatographic properties
DIS	Coefficient of dispersion
DISPER	Computer program for determination of the coefficient of dispersion
PHI	Porosity, fraction
PV	Pore volume, ml
PVIMAX	Maximum number of pore volumes for which the program is to run
Q	Flow rate, ml/hr
VOLIN	Volume of influent solution injected
XLEN	Core length, cm

II. Core and Brine Evaluations

The following methods are utilized for the analysis of the core and brine samples. A pH meter is used to determine the pH of the influent and effluent. The inductively coupled plasma (ICP) spectrometer is used for elemental analysis of core and brine samples. The elemental analyzer is used for the microdetermination of carbon, hydrogen, and nitrogen compounds. The SEM and x-ray diffraction units are used to further define the roles of clays in the experiment.

Inductively Coupled Plasma Analytic Methods¹⁷

Summary of Method

The method describes a technique for the simultaneous or sequential multi-element determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency ICP. The spectra are dispersed by a grating spectrometer and intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate corrections made.

Reagents and Standards¹⁷

Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

1. Acetic acid, conc. (sp gr 1.06).
2. Hydrochloric acid, conc. (sp gr 1.19).

3. Hydrochloric acid, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 ml deionized, distilled water and dilute to 1 liter.
4. Nitric acid, conc. (sp gr 1.41).
5. Nitric acid, (1+1): Add 500 ml conc. HNO₃ (sp gr 1.41) to 400 ml HNO₃ deionized distilled water and dilute to 1 liter.

Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193.¹⁸

Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 hour at 105°C unless otherwise specified.

Sample Handling and Preservation¹⁷

For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order.

Sample Preparation¹⁷

For the determination of dissolved elements, the filtered, preserved sample often may be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat.

Procedure¹⁷

Set up instrument with proper operating parameters. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

1. Initiate appropriate operating configuration of computer.
2. Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions. Flush the system with the calibration blank between each standard. (The use of the average intensity of multiple exposures for both standardization and sample analysis reduces random error.)

3. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ± 5 percent (or the established control limits whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

4. Begin the sample run, flushing the system with the calibration blank solution between each sample. Analyze the instrument check standard and the calibration blank each 10 samples.

5. If it has been found that methods of standard addition are required, the following procedure is recommended:

The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution each of volume V_x , are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s . To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x , and thus c_s is much greater than c_x . To avoid a concentration step, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

Calculation¹⁷

Reagent blanks should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

If dilutions were performed, the appropriate factor must be applied to sample values.

Data should be rounded to the thousandth place, and all results should be reported in mg/l up to three significant figures.

Quality Control¹⁷

Check the instrument standardization as follows:

Analyze an appropriate instrument check standard containing the elements of interest at a frequency of 10 percent. This check standard is used to determine instrument drift. If agreement is not within ± 5 percent of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank at a frequency of 10 percent. The result should be within the established control limits of two standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem, and recalibrate the instrument.

To verify interelement and background correction factors analyze the interference check sample at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

Scanning Electron Microscopy (SEM)¹⁹

The SEM is used to provide visual images and semiquantitative elemental analysis of the core samples. The SEM analyses is conducted utilizing procedures described by Postek, et al.¹⁹ The SEM is of value in determining the sample morphology, surface mineral composition and type and location of clays. Comparison of the core before and after an experiment aids in determining potential rock-fluid interactions and indicates reasons for permeability losses.

The electron microscope characterization of the samples is conducted using an International Scientific Instrument Super III A SEM equipped with a Princeton Gamma Tech System III Energy Dispersive Spectrometer (EDS). The EDS is used to obtain elemental analyses of the core surface.

The SEM is equipped with a secondary electron detector and a Robinson backscatter electron detector. In general when the secondary detector is used, the specimen must be coated with a thin layer of metal such as gold or gold/palladium to avoid electrically charging the sample which produces bright spots on the image. Metallic plating of the sample increases the sample-handling time and introduces the possibility of sample distortion from the metal coating. Sample distortion is partially overcome by using a lower accelerating voltage, but this results in loss of resolution, and it also interferes with the use of the EDS system for elemental analyses. The Robinson backscatter electron detector eliminates artifacts due to the electrical charging of the sample, reduces edge highlights, and gives resolution capability similar to the secondary detector while providing better imaging of difficult samples.

The samples used for SEM/EDS analyses were prepared from small chips of the rock to provide a fresh surface for analysis.¹⁹ The samples should be examined at a low magnification (50X) to obtain an overview of their general characteristics and clay distribution. After identification of significant features such as clay particles and pore throats, the magnification is increased sufficiently to show detailed features of interest, and a photograph is taken. The same procedure is used for EDS analysis while making certain that the image in question is sufficiently magnified to eliminate interference from adjacent features.

X-ray Diffraction Analysis (XRD)²⁰

The interpretation of x-ray diffractograms requires several steps during which the peaks of the diffractogram are converted into significant geologic data.¹⁷ The following steps are followed for mineral identification:

1. Measurement of molecular plane repeat distances (d-spacings).
2. Identification of mineral species.
3. Semiquantitative interpretation of mineral abundance.

Sample Preparation

1. Place ~15 g of rock sample between several layers of paper (Kimwipes).
2. Crush sample (do not pulverize) with hammer to pass thru a No. 40 (425 micron) sieve.
3. Weigh 10 g of the sample to the nearest 0.01 g into a clean 600 ml stainless steel beaker.
4. Add 300 ml of deionized water (DIW) to the beaker, stir, and then place under the sonic dismembrator (setting 60) for ~ 30 sec.
5. Pour half of the supernatant solution in the beaker through a wetted 30-micron wet-sieve atop a 400-ml clean glass beaker. A second, separate sieve/beaker set-up is helpful for speeding up this step.
6. Add ~ 50 ml of DIW to the remaining dispersion in the metal beaker; sonicate, and pour off about half of the supernatant into the wet-sieves, collecting the combined filtrates. Wash the material on the sieve with DIW.
7. Repeat step 6 until the supernatant in the metal beaker is clear.
8. Quantitatively transfer, using a squeeze bottle filled with DIW, the remaining material in the metal beaker to the wet-sieves. Wash the material on the screens with DIW. Retain the filtrates (<30 micron material) in the beakers.

9. Quantitatively transfer, using a squeeze bottle, the material (>30 microns) on the sieves to a Teflon evaporating dish. Decant excess water from the dish. Dry this fraction of the sample at 100° C overnight. Cool and weigh material.
10. Vacuum filter onto a porous (0.5-micron) stainless steel sample plate sufficient filtrate (<30 micron material) to obtain a thin, uniform cake of clay material on the plate. The filtrate should be stirred in order to suspend the clays and added nearly dropwise to the filter to assure that a representative sample is collected on the plate. Save the remaining <30 micron sample in the beakers.
11. Dry the plate (containing <30 micron sample) for 1 hr at 300° C, and cool in a dessicator.
12. Attach the sample plate to a glass slide.
13. Obtain the x-ray diffraction pattern for this sample from 2°-37°, 2 θ .
14. Remove the sample from the glass slide and place in an ethylene glycol chamber at 60° C overnight.
15. Obtain the XRD scan on this glycolated sample (2°-37°, 2 θ).
16. Remove the plate from the glass slide and place it in the muffle furnace at 600° C for 1 hr. Cool the sample in a dessicator.
17. Obtain the XRD scan on the sample (third scan).
18. If the XRD patterns for the <30 micron fraction are of poor quality (peaks small, broad and/or unresolved), centrifuge the remaining filtrate at 1000 RPMS for 3 min. to obtain the <2 micron size fraction (supernatant), and follow steps 10 thru 17.

Semiquantitative Interpretation of Mineral Abundance²⁰

The quantitation of x-ray diffraction data is complicated due to the many interpretations and uses of the spectra generated. A semiquantitative peak-height ratios procedure is described.

Peaks are measured relative to a base line that must be drawn by hand before measurement. A typical base line for the silicate clay fraction is not a straight line. Thus it rises sharply toward the low angle region of the pattern and also forms a very broad swell beneath the 3.35Å (26.6° 2 θ) quartz peak. In general, the base line is a smooth curve along the base of the peaks. Its exact shape varies and is a nonsystematic source of error in quantitative work based on peak heights or peak areas.

Once the baseline is drawn, the vertical distance from the base line to the apex of the critical peak is measured. A simple division then gives the peak-height ratio. This value is a function of the relative quantities present.

It is more accurate to compare peak areas instead of peak heights. Spacing for identification of specific minerals is found in table B-2.

Calculations

A calculation for a sample containing kaolinite, chlorite, illite and montmorillonite clays is described below:

Total Clays:

$$\leq 425\mu\text{m weight} = \frac{\text{clay weight}}{x}; \text{clay weight} = \leq 425\mu\text{m} - \geq 30\mu\text{m}$$

$$\frac{\text{total clay (diffractogram)}}{100} = \frac{x}{y}$$

Peak Identification

$$K + C = \frac{\frac{h \ 7 \text{ \AA} (300^\circ \text{ C})}{2.5}}{\frac{h \ 7 \text{ \AA} (380^\circ \text{ C})}{2.5} + h \ 10 \text{ \AA} (300^\circ \text{ C})} \times 100$$

$$K = \frac{h \ 3.59 \text{ \AA} (300^\circ \text{ C})}{h \ 3.59 \text{ \AA} (300^\circ \text{ C}) + 3.54 \text{ \AA} (300^\circ \text{ C})} \times \% K + C$$

$$C = (\% K + C) - \% K$$

$$I + M = \frac{h \ 10 \text{ \AA} (300^\circ \text{ C})}{\frac{h \ 7 \text{ \AA} (300^\circ \text{ C})}{2.5} + h \ 10 \text{ \AA} (300^\circ \text{ C})} \times 100$$

$$I = \frac{h \ 10 \text{ \AA} (\text{EG}) \frac{h \ 7 \text{ \AA} (300^\circ \text{ C})}{h \ 7 \text{ \AA} (\text{EG})}}{h \ 10 \text{ \AA} (300^\circ \text{ C})} \times \% I + M$$

$$M = (\% I + M) - \% I$$

- h = height, mm
- K = kaolinite
- C = chlorite
- I = illite
- M = expandable materials (montmorillonite)
- EG = ethylene glycol pattern
- x = % total clay in sample
- y = % of each clay type in total sample

TABLE B-2. - Spacings for mineral identification²⁰

d (Å) Spacings for Aggregate Minerals		
d(Å)	Mineral	Notes
* 15.0-12.5	Mont. Group (Smectite)	varying degrees of hydration
14.5-13.5	Chlorite	
* 14.5-13.5	Vermiculite	fully hydrated
* 12.5-12.0	Vermiculite	partially hydrated
* 10.5	Attapulgite	(palgorskite)
* 10.1	Illite	
* 10.1-9.0	Micas	muscovite, biotite, phlogopite
* 9.3	Talc	
* 8.5-8.4	Amphibole	hornblende, actinolite
* 7.56	Gypsum	
* 7.36	Serpentine	antigorite, chrysotile
* 7.5-7.2	Halloysite	metahalloysite (2H ₂ O)
* 7.15	Kaolinite	
* 7.2-7.0	Chlorite	iron-rich chlorites to 6.78Å°
6.65	Orthoclase	"high" K-feldspar
6.45	Microcline	"low" K-feldspar
6.55-6.38	Plagioclase	anorthite to albite
* 5.61-5.57	Analcite	
* 4.85	Gibbsite	
4.79-4.69	Chlorite	
* 4.50-4.45	Clay 020-040	mainly kaolinite & smectites
4.37	Gibbsite	
4.27	Gypsum	
4.26	Quartz	and K-feldspar 4.24-4.21 Å

(*Peaks used for quantitative analysis)

III. Analysis of Phenols and Phenol Degradation By-Products

To ensure adequate quality control of experimental results, ASTM method D2580-83, Phenols in Water by Gas Liquid Chromatography and ASTM method 2908-74, Measuring Volatile Organic Matter in Water by Aqueous-Injection Chromatography, will be used as guidelines for evaluation 1,2-dichloroethane.¹⁸ The use of these methods will also incorporate EPA methods and other applicable guidelines:

1. ASTM D1129 - Definition of Terms Relating to Water,¹⁸
2. ASTM D1193 - Specification for Reagent Water,¹⁸
3. ASTM E200 - Methods for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analyses,¹⁸
4. ASTM E260 - Recommended Practices for General Gas Chromatograph Procedures,²¹
5. ASTM E355 - Recommended Practices for Gas Chromatography Terms and Relationships,²¹
6. Section III-Saline and Brackish Waters, Seawater and Brines, pp. 531-583,¹⁸
7. Properties of Reservoir Rocks: Core Analysis,¹¹ and
8. API Recommended Practices for Analysis of Oil-Field Waters.²⁰

The use of these guidelines will ensure quality control in the laboratory experiment and in the resultant data interpretations. Typical operating conditions for the gas chromatograph are found in table B-3. A statistical survey of bias achieved, using these operating conditions for samples prepared in reagent water and a matrix water, is described in appendix C.

Using ASTM D2580-83, elution of characteristic phenols occur in the following order:

1. o-chlorophenol
2. phenol and o-cresol
3. m- and p-cresol
4. 2,3-, 2,4-, 2,5- and 2,6-dichlorophenol
5. m- and p-chlorophenol, and
6. 3,4-dichlorophenol.

The test method may be applied to waste water or concentrates that contain 1 (one) mg/l or more of phenol compounds. Typical precision, bias and confidence levels for analysis of phenols or its derivatives are presented in appendix C.

TABLE B-3. - Typical operating conditions for chromatographic columns¹⁸

Column and Packing	Column number		
	1	2	3
	3-m by 3-mm (10-ft by 1/8-in.) SS, 20% Carbowax 20M-TPA, 60/80 Chromosorb W-HMDS	1.5-m by 3-mm (5-ft by 1/8-in.) SS, 5% FFAP, 70/80 Chromosorb W	1.5m by 0.53mm Fused silica, Bonded FSOT, Polyethylene Glycol Ester
Carrier gas	helium	helium	helium
Carrier gas flow, ml/min	25	35	30
Temperature, °C:			
Injection port	250	205	250
Column	210	147	150
Hydrogen for detector, ml/min	25	25	30
Chart speed, in.(mm)/h	12(305)	12	12
Sensitivity, mV	1	1	1
Electrometer range	1	0.1	1
Attenuation	1	1	16
Sample vol, μ	1	1	0.3

**APPENDIX C. - PRECISION AND BIAS STATEMENTS FOR
THE VARIOUS ANALYTIC TECHNIQUES**

TABLE C-1. - Atomic absorption precision and bias statements

<u>Element</u>	<u>Precision/Bias</u>			<u>Reference</u>
Aluminium	True value	Mean value	% Bias	(17)
	1,004	1,003	-0.1	
	500	463	-7.4	
Calcium	71.0	70	-2.2	(17)
	2.8	2.9	4.7	
Magnesium	True value		Standard deviation	(17)
	2.1		±0.1	
	8.2		±0.2	
Potassium	1.6		±0.2	(17)
	6.3		±0.5	
Sodium	8.2		±0.1	(17)
	52.0		±0.8	

TABLE C-2. - ICP precision and accuracy data¹

Element	Sample 1			Sample 2			Sample 3		
	True value, $\mu\text{g/l}$	Mean Reported value, $\mu\text{g/l}$	Mean percent, RSD	True value, $\mu\text{g/l}$	Mean Reported value, $\mu\text{g/l}$	Mean percent, RSD	True value, $\mu\text{g/l}$	Mean Reported value, $\mu\text{g/l}$	Mean percent, RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

TABLE C-3. - GC accuracy and bias in reagent water¹⁸

	Amount Added, mg/l	Amount Found, mg/l	$\pm$ Bias, mg/l	$\pm$ % Bias	Statistically Significant (95% Confidence Level)
Phenol	120.3	115.7	-4.6	-3.8	No
	24.1	22.4	-1.7	-7.0	Yes
	7.2	7.7	+0.5	+6.9	Yes
p-Cresol	120.5	116.9	-3.6	-3.0	No
	24.1	23.1	-1.0	-4.1	No
	7.2	6.8	-0.4	-5.6	No
p-Chlorophenol	120.5	115.4	-5.1	-4.2	No
	24.1	23.8	-0.3	-1.2	No
	7.2	7.5	+0.3	+4.2	No
2,5-Dichlorophenol	112.6	106.0	-6.6	-5.9	No
	22.7	21.0	-1.7	-7.5	No
	6.7	6.1	-0.5	-8.9	No

TABLE C-4. - GC accuracy and bias in matrix water¹⁸

	Amount Added, mg/l	Amount Found, mg/l	$\pm$ Bias, mg/l	$\pm$ % Bias	Statistically Significant (95% Confidence Level)
Phenol	120.3	119.6	-0.7	-0.6	No
	24.1	23.1	-1.0	-4.1	No
	7.2	7.3	+0.1	+1.5	No
p-Cresol	120.5	120.0	-0.5	-0.4	No
	24.1	24.2	+0.3	+1.2	No
	7.2	7.1	-0.1	-1.3	No
p-Chlorophenol	120.5	113.8	-6.7	-5.6	No
	24.1	24.4	+0.3	+1.2	No
	7.2	7.7	+0.5	+6.5	No
2,5-Dichlorophenol	112.6	116.9	+4.3	+3.8	No
	22.7	21.7	-1.0	-4.4	No
	6.7	6.2	-0.5	-7.5	No

**APPENDIX D. - QUALITY ASSURANCE PROCEDURES FOR THE
EXPERIMENTAL PORTION OF LABORATORY RESEARCH ON
ON
DEGRADATION, INTERACTION AND FATE OF
WASTES DISPOSED BY DEEP-WELL INJECTION**

Introduction

Deep-well disposal of hazardous wastes and EOR chemicals involve their injection into subsurface reservoirs. Injection operations pose potential pollution threats to zones that contain potable water. It is necessary to understand:

1. the abiotic and biotic reactions that can cause the wastes, and their by-products to degrade;
2. the chemical interactions that can occur between the indigenous fluids and rocks present in the injection and confining zones with the injected hazardous wastes and EOR chemicals; and
3. the ultimate fate of the wastes injected into deep wells.

This section outlines the quality assurance (QA) plan for the project entitled Degradation, Interaction and Fate of Wastes Disposed by Deep-Well Injection. NIPER conducts testing using state-of-the-art instrumentation and standardized EPA, ASTM or other well recognized analytical methods. Data were validated using a well documented IIT Research Institute quality assurance program.

Project Description

The objective of this project was to develop a protocol to determine the fate of hazardous wastes and their degradation compounds by means of simulating subsurface injections into the subsurface formation rock samples and assess the environmental impact. The laboratory studies were conducted using a dynamic flow-through system at simulated reservoir temperatures and pressures. The hazardous wastes used in the first series of tests to demonstrate the protocol were phenol, and 1-2-dichloroethane. The core samples were from the Frio formation (1.5 in. x length desired). Initial test conditions were conducted with a neutral pH system which provide a baseline for subsequent testing of acidic and basic systems.

This research generates results for use in predicting the ultimate fate of hazardous wastes or other fluids injected into the subsurface through deep wells. Reactions that can be used in predictive models include adsorption, oxidation, reduction, precipitation, coprecipitation, dissolution, ion exchange, hydrolysis, and neutralization.

Project Organization and Responsibilities

Organization

The organizational structure as required for this project is shown in figure D-1.

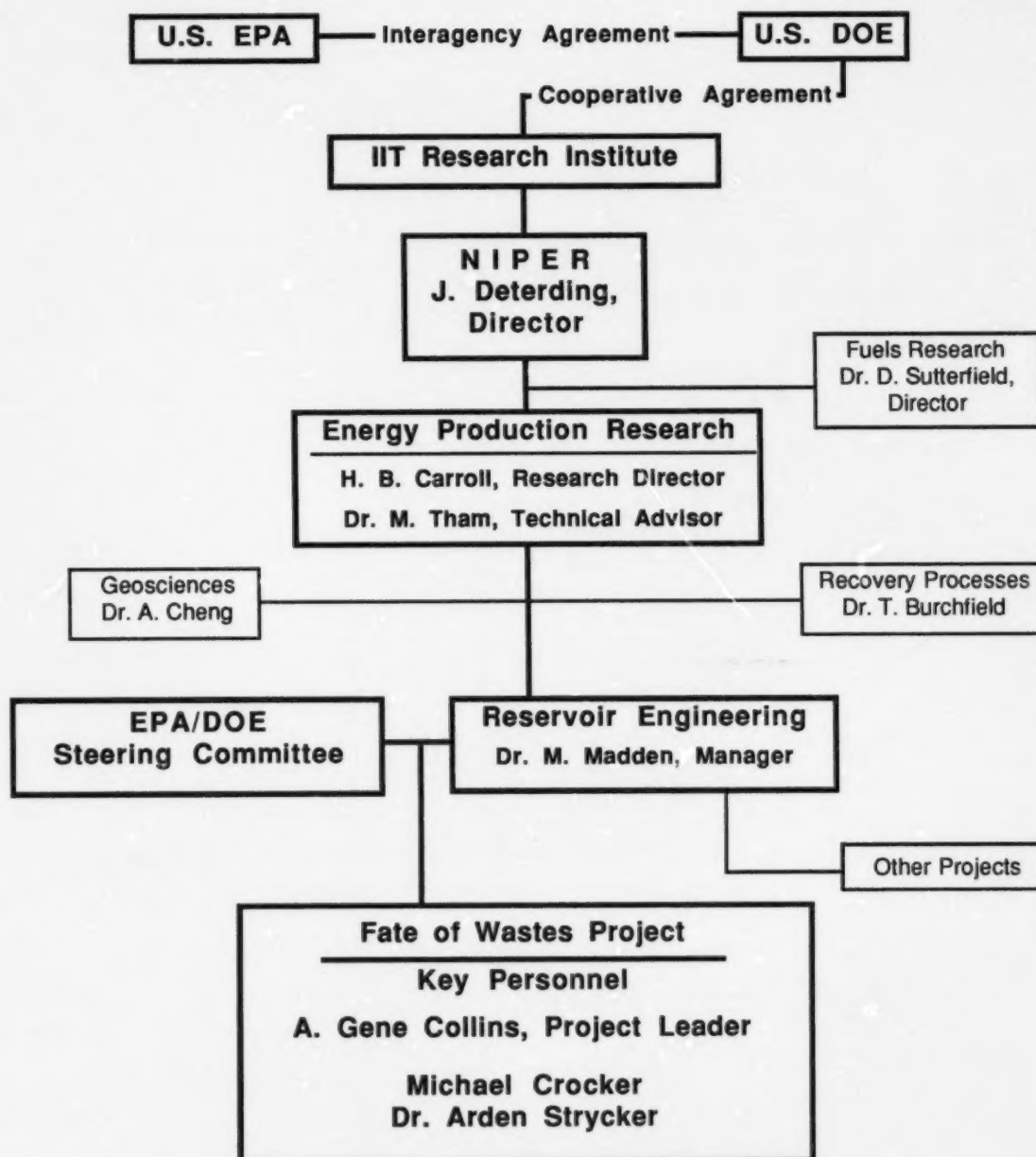


Figure D-1. Degradation, Interaction, and Fate of Wastes Disposed By Deep-well Injection Phase 2 Project Organization And Management

Key Staff

Dr. Michael P. Madden, Manager of Reservoir Engineering, and A. Gene Collins, Principal Investigator for this project, are responsible for project management. Other NIPER staff who are involved in this project are Michael Crocker, Dr. Arden Strycker, Bill Linville, and technicians as needed.

Coordination With EPA

A. Gene Collins will maintain contact with Alex Crawley of the DOE Bartlesville Project Office and EPA Project Officer Lowell Leach to aid in the overall progress of the project. This information exchange will be on both an informal and formal basis and will include Quarterly Reports and a Final Report.

Quality Assurance Objectives

The National Institute for Petroleum and Energy Research (NIPER), has as its sole responsibility, the reporting of measurement data that are scientifically obtained and statistically documented. Such a responsibility must replace the subjective or nonchalant approach toward generating measurement data with a technically acceptable and systematically correct procedure. The purpose of the document presented herein is to define and document the approaches to be employed to advance and attain such a responsibility. The system is so designed that individuals will follow written and established protocols whenever possible and will document the accuracy and precision of the data by both systematic and calibration and audit analyses. The success of such a practice can only be assured by appropriate laboratory supervision and dedicated management commitment.

The overall program is structured to meet the requirements set forth in the EPA policy statement relating to a National Quality Assurance Program, promulgated in May 1979, and the FDA's Proposed Good Laboratory Practice Standards for Health Effects as it appeared in the Federal Register, July 26, 1979 (Part IV). The quality assurance program outlined in this document covers such aspects as sampling, calibration, and analytical procedures, data collection and reporting, auditing, sampling, shipping, storage, computational and data validation and documentation, and management responsibility.

The basic objective to be attained by the implementation and conformance to the Quality Assurance Program presented herein is the scientific documentation of the quality of the measurement data being generated within our research laboratories. This objective is realized by:

- critically evaluating and validating each step in an overall analytical protocol;
- reviewing all data and procedures on a regularly scheduled basis;
- assessing and correcting any actual or potential problem areas; and
- compiling documentation of performance and management review.

Analytical and Experimental QA Procedures

Core Sample Use/Preparation

The Frio formation core samples were used for the initial studies. Further discussions and research are required before full documentation can be presented in this section.

Organic Contaminant Selection/Preparation

As noted previously, the hazardous wastes to be used in the first series of experiments were to be phenol and 1-2-dichloroethane. The selected hazardous wastes were purchased as a pure, reagent grade chemicals. The initial tests were conducted at a neutral pH. The hazardous wastes were quantitatively prepared using an injection method to simulate typical subsurface saline aquifers such as the Frio.

These solutions were stored at 40° F to preserve sample integrity during the experimentation. Before each series of experiments, the test solutions were monitored to assure sample integrity. The composition of each individual solution were made to assure knowledge of potential chemical interaction that could occur during the experimentation.

Analytical Procedures

To analyze for adsorption or transformation of the hazardous wastes a Hewlett-Packard 5730A gas chromatograph, equipped with flame ionization and thermal conductivity detectors, was used. The techniques used for the gas chromatography followed the procedures established by the EPA Environmental Monitoring and Support Laboratory.

The analysis of inorganic constituents were made utilizing a Perkin-Elmer Model 604 atomic absorption (AA) unit and a Perkin-Elmer Model 5500 inductively coupled plasma spectrometer (ICP).

To ensure sample testing integrity, careful consideration and detail was given to the use of standard solutions, reagents and calibration. Typically, scandium is used as an internal standard with ICP analysis.

An International Scientific Instrument scanning electron microscope (SEM) was used for visual observation of the distribution and morphology of clays present within the core material. Elemental analysis was determined using the Princeton Gamma Tech energy dispersive spectrometer.

Where practical, standard analytical procedures were selected and used, to expedite comparison of results obtained from different experiments. Chemical analyses of aqueous solutions, e.g. brines, were for major anions and cations, pH, total alkalinity, and total organic acids, and other organic compounds. Analysis techniques followed standardized procedures documented in the following analytical compendia:

1. Annual Book of ASTM Standards, Water and Environmental Technology, vols. 11.01, 11.02, 11.03, 11.04, 1986, American Society for Testing and Materials.
2. Methods for the Chemical Analysis of Water and Wastes, 1983, U.S. Environmental Protection Agency.
3. Methods for Organic Chemical Analysis of Municipal and Industrial Waste Waters, EPA-600/432-057.
4. Standard Methods for the Examination of Water and Wastewater, 16th ed, 1985, Amer. Public Health Assoc./Amer. Water Works Assoc./Water Poll. Control Fed.
5. API Recommended Practice for Analysis of Oil-Field Water, RP 45, 1981, American Petroleum Institute.

This is a research project and analytical methods not found in standard compendia may arise, necessitating the development of new or modified analytical procedures. New analytical techniques will be described in writing and reported to the EPA project officer for approval. Whenever they are used, nonstandard analytical procedures will be identified in laboratory notebooks, and shall be fully described in the reports from this project.

Sample Handling

Since these experiments did not require exhaustive handling of samples, an elaborate tracking mechanism was not required. However, to ensure quality control, each formation sample and organic contaminant tested was assigned a unique number for a chain of custody for future reference.

Instrument Maintenance

To ensure proper instrumental operation for experimental analyses, the following preventive maintenance schedule was in place.

Inductively Coupled Plasma Spectrometer

<u>Function</u>	<u>Scheduled Maintenance</u>
Water filter	12 months
Inlet lines	12 months
Drain tubing	12 months
Mirror	12 months
Filter	3 months
Peristaltic pump tubing	1 month
Torch	1 month

Gas Chromatograph

<u>Function</u>	<u>Scheduled Maintenance</u>
Air filter	6 months
Detectors	Poor signal
Column	Poor resolution
Septum	Daily
Scrubbers	2-6 months

Although other instrumentation used for this project will only be on an intermittent basis, the same degree of quality control will be maintained.

Corrective Action

Since laboratory personnel are more closely associated with all aspects of the experimentation and instrumentation, they will be the first to note a need for corrective action in either area. Some corrective actions may be avoided by normal maintenance schedules as noted. However, it was still the responsibility of the laboratory personnel to note variations in temperature, pressure, loss of resolution or loss of fluids that were not expected.

All aspects of each individual experiment and analytical test will be closely monitored and logged. A. Gene Collins had the responsibility of noting areas of major problems and defining corrective procedures.

APPENDIX E. - POLICY STATEMENT FOR THE NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH

It is the policy of the National Institute for Petroleum and Energy Research to establish and maintain a program of quality assurance (QA) and quality control (QC) to ensure that all data collected are scientifically obtained and statistically documented. QA program requirements cover all activities supported or required by the various government agencies that generate measurement data.

Management has the overall responsibility for implementing the quality assurance requirements within NIPER. The responsibility for monitoring QA activities within NIPER is delegated to Greg Steele, QA Officer.

The objective of the QA program is to assess, ensure, and document that all data collected, stored, and reported are scientifically valid and of known precision and accuracy. This objective is realized by:

- critically evaluating and validating each step in an overall analytical protocol;
- reviewing all data and procedures on a regularly scheduled basis;
- assessing and correcting any actual or potential problem areas; and
- compiling documentation of performance audits and system audits.

Measurement activities within NIPER will be performed in conformity with the approved QA project plan on file with the QA Officer.

The QA program for NIPER will meet the following requirements:

1. The QA functions will be carried out by the Quality Assurance Officer.
2. A QA Committee will assist the QA Officer in implementing the QA policy.
3. All data generated will meet the following requirements:
 - a. Analytical methods and procedures used in measurement and monitoring will conform to EPA, NIOSH, AOAC, and ASTM approved methodology, insofar as possible. All measurement methods will be fully documented and include quality control (QC) procedures.
 - b. Quality assurance project plans, standard operating procedures, and protocols will be developed for all measurements and monitoring activities.
 - c. Plans for the intended use of the data and the associated acceptance criteria for data quality will be developed before the data collection effort begins.

- d. All data will achieve the level of quality necessary for the intended use of the data.
 - e. QA/QC project plans will be developed prior to, and implemented at, the onset of each data collection effort to suit the precise QA needs of that effort.
 - f. All reported data will be of stated precision, accuracy, and representativeness.
- 4. Data processing procedures will be documented, reviewed, and revised as necessary to meet data quality requirements. Data will be validated according to specified criteria.
 - 5. QA management will include a regular schedule of performance and system audits, determined by the QA Officer.
 - 6. The QA Officer will work with project personnel, and will develop and implement a mechanism for timely corrective action.
 - 7. The QA Officer will report on a regular basis to the Deputy Director on QA progress, problems, and data quality assessments. The QA program plan will be updated as necessary.

Quality Assurance Management

The Quality Assurance Program at NIPER is a function under the direction of Don Ward, Deputy Director. He has assigned the responsibilities for monitoring the Quality Assurance activities to Greg Steele.

Responsibilities and Authority of Quality Assurance Officer (DQA0)

The QAO's role in the Quality Assurance Program is primarily monitorial in nature. In this role he must act as an independent and impartial auditor to ensure that all aspects of the Quality Assurance Program are being properly addressed by project personnel. Accordingly, Greg Steele, the QAO, bears the responsibility to:

- review all standard operating procedures and analytical protocols for each project plan;
- provide reviews and document results of all audit samples;
- maintain files of all the quality control and quality assurance procedures;
- monitor all quality control practices to ensure conformance with approved policy;
- support project personnel in the acquisition of equipment, glassware, supplies, and reagents to meet the requirements of the analytical protocol;
- report all deviations from established analytical protocols to project personnel and the Deputy Director and assist in correcting deficiencies; and
- continually review and upgrade quality assurance practices.

Project Audits

Performance audits and system audits will be conducted on each measurement program as determined by the QAO. The purpose of these audits is to assess the effectiveness of QA on each project. The audits will be performed at intervals adequate to ensure the integrity of the measurements.

Performance audits will be conducted using available materials or devices for the measurements to be made. The QAO is responsible for incorporating performance control samples or devices into the measurement system in a manner that permits it to be indistinguishable from test samples or devices. The level of activity of such samples will be determined on a project basis. Upon completion of the analysis of the audit sample, a Standard Quality Assurance Unit Control (Audit) Sample(s) report form is prepared by the QAO and submitted to the Deputy Director, Quality Assurance Committee, and Project Leader. Appropriate remedial action will be initiated immediately if warranted. A standard form is attached.

System audits will include inspection and evaluation of personnel, facilities, and procedures without requiring actual performance data of a known reference material. The Quality Assurance Officer conducts inspection at intervals adequate to ensure the integrity of the measurement method. A standard form for the Quality Assurance unit inspection is attached. Specific system audit forms will be prepared for each measurement method.

Document Control

QA project plans will be prepared according to the document control format described in Section 1.4.1 of the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume 1 (EPA-600/90-76-005). This system uses a standardized indexing format and provides for convenient replacement of pages that may be changed within the technical procedure descriptions. The indexing format includes, at the top of each page, the following information:

- Section No.
- Revision No.
- Date (of revision)
- Page

QUALITY ASSURANCE UNIT CONTROL (AUDIT) SAMPLE(s) REPORT

DATE: _____
PROJECT: _____
TITLE: _____
QUALITY ASSURANCE OFFICER: _____
PRINCIPAL INVESTIGATOR: _____
SPONSOR: _____

AUDIT SUMMARY

Analyte	Audit Value	Analyzed Value	Percent* Difference Limit ±5%

$$\text{* Percent Difference} = \frac{\text{Analyzed Value} - \text{Audit Value}}{\text{Audit Value}} \times 100$$

cc: Quality Assurance Unit
Principal Investigator
Management

QUALITY ASSURANCE UNIT INSPECTION REPORT

DATA: _____

PROJECT: _____ SPONSOR: _____

TITLE: _____

_____ COMPOUND: _____

QUALITY ASSURANCE OFFICER: _____ TEST SYSTEM: _____

_____ LENGTH OF STUDY: _____

PRINCIPAL INVESTIGATOR: _____

1. Protocol submitted? Yes___ No___
2. All revisions authorized? Yes___ No___
3. Standard Operating Procedures? Yes___ No___

Comments on deficiencies:

1. _____
2. _____
3. _____

Items Inspected	Findings and Recommendations
Facilities:	
Instrument Logbooks:	

A document control or cataloging system will be devised where documents and other information on file are cross indexed by number and key work such that ready access to all information is possible. Distribution lists of all personnel who need to receive QA reports and information will be maintained as a part of the document control system.